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UNITED STATES DEPARTMENT OF COMMERCE

Journal of Research

of the

National Bureau of Standards

Vol. 33, No. 4 October 1944

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Journal of Research

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Volume 33, Number 4

October 1944

[Published with approval of the Director of the Budget]

UNITED STATES
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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1606

Part of Journal of Research of the National Bureau of Standards, Volume 33, October 1944

REVIEW OF RECENT ABSOLUTE DETERMINATIONS OF THE OHM AND THE AMPERE

By Harvey L. Curtis

ABSTRACT

In the decade preceding 1944 there were published the results of eight determinations of the absolute ohm and seven of the absolute ampere. These determinations were made in the national standardizing laboratories of England, France, Germany, Japan, and the United States. However, only preliminary results of some of the researches have been published, and one value of the absolute ampere was obtained in an experiment that was originally developed for another purpose. Hence to obtain the most probable values of the absolute ohm and ampere, it is necessary to ignore some of the published results and to consider some of those remaining as more reliable than others. A critical analysis has been prepared of each of the determinations, and this analysis has been used as a basis for weighting the results.

The most probable value of the absolute ohm is given by the relation

1 mean international ohm = 1.000 490 absolute ohms.

The mean deviation from the mean of the results used in obtaining this value is only 14 parts per million. Further confirmation of the probability of this result is shown by the agreement with the results of two other recent compilers of the absolute-ohm determinations.

The most probable value of the absolute ampere is given by the relation

1 mean international ampere = 0.999 853 absolute ampere.

The mean deviation from the mean of the three results used in obtaining this value is 3 parts per million. Other recent compilers. however, have given larger values, one, 27 parts per million larger, and the other, 119 parts per million larger.

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I. INTRODUCTION

The values of the absolute electrical units are all based on absolute determinations of the ohm and the ampere. The absolute determinations of these two units that have been made in the national laboratories during the past decade are more accurate that those made at any previous time. The national laboratories at which the measurements were made are the National Physical Laboratory, England, (NPL); Laboratoire Central d'Électricité, France, (LCE); Physikalisch-Technische Reichsanstalt, Germany, (PTR); Electrotechnical Laboratory, Japan, (ETL); and the National Bureau of Standards, United States, (NBS). But the recent determinations are not all of equal accuracy, so that the most probable value cannot be obtained merely by taking a mean of all the published values. In fact, only by making a critical analysis of each determination can one judge the relative importance of the different values that have been obtained.

Some definite principles have been used in determining the weight to be applied to the different determinations of the ohm and the ampere. In general, a result which has been classed as preliminary in the article which describes the experimental work is given zero weight. There is one exception, which will be explained in connection with the analysis of the work. One other result has been given zero weight because much more precise results have now been obtained by the same experimenters. Other results have been weighted according to the judgment of the author of this article, giving a weight of 5 to those which seem to be most accurate, and smaller weight to results that are less reliable.

The author realizes the difficulty of making a critical review of a field in which the work of himself and associates must be compared with that of others. This difficulty is not as great as in some fields, because there has been cordial cooperation among all who are working on the values of the absolute electrical units. Each laboratory has welcomed visits from other investigators working in this field. The author has visited all the laboratories where the investigations have been made, except those in Japan.

The results of all recent evaluations of the absolute electrical units have been expressed in terms of the so-called "international ohm" and the "international ampere." Both of these units have slightly different values in different laboratories. The differences between the units of the national laboratories for the same quantity have

always been too small to be considered except in measurements of the highest precision. Since the measurements to be reviewed in this paper are of an accuracy which requires that these differences shall be taken into account, a brief statement concerning the establishment and maintenance of the international units is necessary.

The international ohm as established in 1893 was "represented by the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice, 14.4521 grammes in mass, of a constant cross-sectional area and of a length of 106.3 cms." The mass of mercury was chosen to give a cross-sectional area of 1 square mm and a length of 106.3 cm. These dimensions gave to the international ohm a value which agreed with the absolute ohm as nearly as could be determined from the absolute measurements that had been made up to that time. The international ohm was maintained by means of the mercury ohm for about 20 years. Gradually wire-resistance standards were developed that were so permanent that the international ohm could be maintained more precisely by them than by reestablishing the unit every few years by means of measurements on the mercury ohm. Hence during the last two decades not one of the national laboratories has reestablished its unit for the international ohm by making measurements upon the mercury ohm. Instead each laboratory maintains its international ohm by means of wire resistance standards, the values of which were originally established by reference to the mercury ohm. There are slight differences between the values of the international ohm of the different national laboratories. These differences have been determined on several occasions at the International Bureau of Weights and Measures. Hence the results of all recent measurements of the absolute ohm can be expressed in terms of the mean international ohm, the value of which is the mean of the values of the international ohm as maintained at the important national laboratories. The mean international ohm is herein assumed to have remained constant during the last decade. There is no longer need of making measurements on the mercury ohm, since the absolute ohm can now be used to establish and maintain the unit of resistance with greater accuracy than can be obtained by using the mercury ohm.

The international ampere was defined as the "unvarying current which, when passed through a solution of nitrate of silver in water * * * deposits silver at the rate of 0.001118 grammes per second." The international ampere so defined, in connection with the international ohm has been used to determine the electromotive force of a standard cell. Routine laboratory measurements of current in international amperes have always been made by reference to a standard resistor and a standard cell. Since 1911 the National Bureau of Standards has maintained the international volt by means of a group of standard cells. Similar methods have been used by other national laboratories, at least during the last decade. The results of determinations of the absolute ampere made in the last decade have been expressed in terms of the international ohm and international volt as maintained in the national laboratories where the determination was made. These national units can be reduced to a common basis by the comparisons of standard resistors and standard cells which have been carried out at the International Bureau of Weights and Measures. The results for 1933, 1935, 1937,

and 1939 have been published in the Procès-verbaux of the International Bureau. It is assumed that the mean international ampere (the mean of six national laboratories) has remained constant during last decade.

II. RÉSUMÉ OF ABSOLUTE-OHM DETERMINATIONS

Eight independent researches on the value of the absolute ohm have been reported during the last decade. In order to evaluate properly the different results, the following analysis of the eight determinations has been made, taking them in chronological order.

(a) 1936: CURTIS, MOON, AND SPARKS AT NBS[1]

In the method employed in this investigation the value of a self inductance in international henrys was compared with its value in absolute henrys. The ratio of these values is the same as the ratio of the value of a resistance in international ohms to its value in absolute ohms. The inductance of a self inductor in international henrys was obtained by electrical measurements which involved the mean solar second and the international ohm. In the electrical measurements, the self inductance was compared by a bridge method with a capacitance and a resistance, using low-frequency alternating current; and then the capacitance was measured in terms of resistance and time, using a pulsating current. The error in the electrical measurements was probably only a few parts in a million. A large number of electrical measurements were made on three helical inductors having different dimensions and different values of inductance.

The inductance of each helix in absolute henrys was computed from its measured dimensions and the permeability of the surrounding medium. The mechanical measurements of the diameters, which were very uniform, were made with high accuracy. The average pitch of each helix was accurately measured, but the measurements showed that the pitch was not exactly uniform for any of the helices. The basic formula used in computing the inductance in absolute units assumed that the winding was of uniform pitch, although the formula was extended by introducing terms to correct for the displacement of one or more complete turns from a true helical form. The actual helix did not conform exactly to the conditions required for a precise computation of the inductance, even by the extended formula. For example, there may have been displacements within each turn, which would affect the result more than the average displacement of a turn. These displacements would all tend to increase the inductance over that of a uniform helix. Hence, the computed value of the inductance for each of the three inductors used may have been too small. If this were the case, the result given by the authors was too small. Since their result is the smallest of any of those obtained in the last decade, it seems probable that the effect of irregularities in pitch produced an error in the result. Hence the result of this investigation is given a low weight, despite the fact that all electrical and mechanical measurements were carried out with great care.

[1] H. L. Curtis, C. Moon, and C. M. Sparks, *An absolute determination of the ohm*, J. Research NBS 16, 1 (1936) RP857.

(b) 1936–37: VIGOUREUX AT NPL [1]

Vigoureux used the same apparatus used by Smith [2] in 1914. The fundamental unit in this apparatus was a Lorenz apparatus or homopolar generator for which the induced electromotive force could be computed from measured quantities, namely, the dimensions of the generator, the speed of rotation of its armature, and the current in its field coils. The armature consisted of two disks, each 54 cm in diameter. They were 167 cm apart and connected by a rigid shaft. The field coils for each disk were a pair of short solenoids coaxial with the disk and a short distance from it. The electrical measurements consisted in balancing the induced electromotive force against the fall of potential produced by the field current in a standard of resistance. The value of this resistance was thus determined from the dimensions of the generator and the speed of rotation of its armature.

Vigoureux remeasured all the mechanical dimensions and made 74 sets of electrical measurements. The same methods of making the mechanical measurements were employed as had been used by Smith. The measurement of any individual outside diameter of the helices, which was about 35 cm, was accurate to 0.1 micron (abbreviation μ). However, according to Smith, there were variations of 40μ in the different diameters of one helix, and in the most uniform helix the variation was about 15μ, or 40 parts per million (abbreviation ppm). Individual measurements of the length of the helices, which length was about 16 cm, were accurate to 1μ, or 6 ppm. The pitch, which had a nominal value of 1667μ, had a periodic variation with a total amplitude of about 30μ for the most uniform coil, and 50μ in the most extreme case. The remeasurement showed that, on the average, the diameters had decreased 13 ppm and the lengths increased by 5 ppm.

The electrical measurements were reported in eight groups. The mean of each group varies from the mean of all the groups by a minimum of 5 ppm and a maximum of 13 ppm. Only a single set of coils was available, so that there were no independent checks. Summarizing, the coils were not precisely made, the electrical measurements showed considerable variations even when averaged in large groups and only one set of helical coils was employed. Hence, a low weight has been assigned to the result.

(c) 1937: YONEDA AT ETL [4]

Yoneda compared a fixed standard of mutual inductance, the value of which could be computed from the mechanical dimensions of the inductor, with a variable mutual inductance, using a low-frequency alternating current. This variable was compared with a resistance and capacitance in an alternating-current bridge. Finally, the capacitance was measured in terms of resistance and time by a pulsating current. From this series of measurements, the inductance of the standard was obtained in international henrys. The work has not been described in sufficient detail to permit an evaluation of its merits. The result is preliminary and hence is given zero weight.

[1] P. Vigoureux, *Determination of the ohm by the method of Lorenz*, Nat. Phys. Lab. Collected Researches **24**, 209 (1936–37).

[2] F. E. Smith, *Absolute measurements of a resistance by a method based on that of Lorenz*, Trans. Roy. Soc. (London) [A] **214**, 27 (1914); Nat. Phys. Lab. Collected Researches **9**, 209 (1914).

[4] Rinkichi Yoneda, *Absolute determination of electrical resistance*, Procès-verbaux, Comité International des Poids et Mesures [2] **18**, 178 (1937).

(d) 1937: HARTSHORN AND ASTBURY AT NPL [5]

These authors used the method of Albert Campbell, by which the value of a mutual inductance was determined in international henrys and in absolute henrys. The standard inductor used in this investigation was a Campbell mutual inductor Its value in absolute henrys was computed from the dimensions of the inductor and the permeability of the surrounding medium. The value in international henrys was obtained by a series of electrical measurements that involved a resistance whose value was known in international ohms and a sinusoidal current whose frequency was precisely known.

For making the electrical measurements, a standard resistor and the primary of an auxiliary mutual inductor were connected in series to the source of the sinusoidal current. The secondary of this inductor was connected to the primary of a second mutual inductor. The electromotive force induced in the secondary of this second mutual inductor was balanced against the fall in potential over the standard resistor. Comparisons of the mutual inductances of the auxiliaries with that of the standard mutual inductor and an evaluation of the frequency of the sinusoidal current were required to determine the mutual indutance of the standard in international henrys. The electrical measurements were made with extreme care. The authors gave careful consideration to every suggested source of error and succeeded in devising an experimental technique that apparently made the errors of measurement negligibly small. They made 23 sets of measurements, each of which required 8 separate observations in order to eliminate correction terms. The maximum deviation of the value obtained in any set of observations from the mean was 9 parts per million. The authors estimated that the electrical measurements did not introduce an error of more than 5 parts in a million in the final result, and this conclusion is well supported by the data.

The computed value of the mutual inductance of the standard mutual inductor was not as accurately known as the measured value. The primary winding of the standard consisted of two helices wound on the same marble cylinder and separated by a distance about twice the length of each helix. The secondary was a multilayer coil having twice the diameter of the helices. It was coaxial with the helices and midway between them. The details of the mechanical measurements have not been published, but they have been published for two very similar inductors made by the NPL for the Japanese Government. The first was destroyed in the Tokio earthquake and was later replaced. It will be assumed as a basis for discussion that the variations in dimensions of the inductor retained at the NPL are about the same as the corresponding variations in dimensions of one of the inductors sent to Japan. The ellipticity of each helix was such that in every plane perpendicular to the axis the major diameter was 70 ppm greater than the minor diameter. Also the form on which the two helices were wound was slightly conical, so that the average diameter of one helix was 22 ppm larger than the average diameter of the other. The pitch of one helix was 70 parts in a million less than its nominal value of 1 mm, whereas at the other end it was 600 parts in a million greater than the nominal value, and there were variations in pitch of

[5] L. Hartshorn and N. F. Astbury, *The absolute measurement of resistance by the method of Albert Campbell* Trans. Roy. Soc. (London) [A] **236**, 423 (1937).

30 μ in each helix. A correction of 6 ppm was made in the computed inductance on account of the variations in diameter, and of 16 ppm because of the variation in pitch, but neither of these corrections could be determined with much accuracy. Errors in the dimensions of the secondary and in its location relative to the primary probably did not introduce an error greater than 1 ppm in the computed inductance.

The imperfection in the construction of the inductor might lead to the conclusion that there was considerable uncertainty in the value of the computed inductance. However, the measured difference between the inductance of the NPL standard and that of one of those prepared for the Japanese Government agreed with the computed difference within 5 ppm, and the agreement between the NPL standard and the second Japanese standard was 8 ppm. These agreements in the measured and computed differences do not make certain that the computed inductances are correct, since the same type of systematic errors could have occurred in the measurements upon all three inductors or in the computations of their inductances. The error in the computed inductance may have been more than the 10 ppm estimated at the National Physical Laboratory. Nevertheless, the agreement between the three inductors indicates that the corrections for irregularities are probably correct. It is an excellent piece of work and deserves a high weight.

(c) 1938: JOUAUST, PICARD, AND HÉROU AT LCE [6]

The electrical network employed by Jouaust, Picard, and Hérou was the same as that used by Hartshorn and Astbury but involved different balancing conditions. A new description of the network is required to clarify the difference. A standard resistor and the primary of a mutual inductor were connected in series to the source of sinusoidal current. The resistor was paralleled with another circuit consisting of the primary of a second mutual inductor in series with a moderately high resistance. The electromotive forces induced in the two secondaries were balanced against each other by proper adjustment of the constants of the circuits. The product of the resistances of two standard resistors was equal to the product of the square of the angular velocity of the alternating current, the mutual inductance of the inductor which was connected directly to the a–c source, and the self inductance of the primary of the second mutual inductor. Hence a self and a mutual inductance had to be compared with the self inductance of a standard in the form of a helix approximately 9.5 cm in diameter wound with wire 0.3 mm in diameter, the pitch of the winding being 0.6 mm. The self inductance of this standard was about 18 millihenrys. The diameter of the helix was computed from the measured length of wire at a definite tension required to wind a given number of turns. This computation involved not only the length of wire, but also the elastic constants of the fused quartz form. The variations in diameter were 150 ppm. The pitch, measured on a special comparator, varied by as much as 50 μ from its nominal value of 600 μ. The authors do not estimate the error in the computed inductance.

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[6] R. Jouaust, M. Picard, and R. Hérou, *Determination of the unit of resistance in the cgs electromagnetic system*, Bul. soc. franç. elec. [3] **8**, 1 (1938).

There were 20 determinations in the final series of electrical measurements by which the value of inductance in international henrys was evaluated. Each determination required five different electrical comparisons. The mean variation from the mean was ±20 ppm. The final value is given to 1 part in 100,000. The authors state, "We estimate that the last significant figure can differ from the true value by several units."

The method of measuring the diameter of the primary standard of inductance may have introduced appreciable errors. Also the electrical measurements were difficult and are not given in enough detail to permit an independent analysis. Hence the result has been given a low weight.

(f) 1938: CURTIS, MOON, AND SPARKS AT NBS[7]

The same method was employed in this investigation as was used by the authors in 1936. The principal improvement consisted in constructing an inductor in the form of a helix in which the variations in pitch were much less than in those previously used. The form for the inductor was a glass cylinder, 120 cm long, 35 cm in diameter, having a wall thickness of about 7 cm. In the outside surface a screw thread with a pitch of 1 mm was ground and lapped. In the screw thread was wound a wire having a diameter of 0.72 mm. The variations in the pitch of the winding were so small (the maximum observed was 0.003 μ) that those indicated may have resulted from inaccuracies of measurement rather than from imperfections in construction. The outside diameter of the helix had a maximum variation of 4 μ, or 10 ppm. The average diameter as obtained by one set of measurements differed from that by another independent set by 0.5 μ, or 1.5 ppm, but this was probably caused by uncertainties in the length of the two end standards used. The authors state that the error in the computed inductance is probably less than 4 ppm.

The value of the inductance in international henrys was obtained from 90 sets of observations. The average deviation of the result of each set from the mean of all the sets was 6 ppm. The electrical measurements were not as consistent as those of Hartshorn and Astbury, but the standard inductor of the NBS had much more uniform dimensions. Hence the result of this determination is given the same weight as that of Hartshorn and Astbury.

(g) 1939: ZICKNER AT PTR[8]

The method employed by Zickner was the same as that used by Curtis, Moon, and Sparks. Details of his method have not been published. The result is preliminary and hence given zero weight.

(h) 1939: WENNER, THOMAS, COOTER, AND KOTTER AT NBS[9]

Only a preliminary report has thus far been published. The complete report has been delayed by the war. The author of this

[7] H. L. Curtis, C. Moon, and C. M. Sparks, *A determination of the absolute ohm, using an improved self inductor*, J. Research NBS 21, 375 (1938).

[8] G. Zickner, *On the status of the experiments for the determination of the international ohm in absolute units*, Procès-verbaux, Comité Consultatif d'Electricité, p. E41, 1939 (advance print for Procès-verbaux, Comité International des Poids et Mesures).

[9] F. Wenner, J. L. Thomas, I. L. Cooter, and F. R. Kotter, *Preliminary report on the absolute measurement of a resistance based on the reversal of a direct current in a mutual inductance*, Procès-verbaux, Comité Consultatif d'Electricité, p. E48, 1939 (advance print for Procès-verbaux, Comité International des Poids et Mesures).

digest can give a summary of the method because of his personal contact with the investigators while the work was in progress and because a laboratory report is available to him.

In the method employed in this investigation a direct current was passed through a standard resistor and through the primary winding of a standard mutual inductor. The current through the primary of the mutual inductor was reversed at regular intervals without changing the current through the resistor. A commutator reversed the connections to the secondary of the mutual inductor in such a way that the pulses of induced electromotive force were always in the same direction. This rectified electromotive force was balanced against the constant potential drop through the resistor. A direct-current galvanometer was used to indicate the balance. When a balance was obtained, the equation for computing the resistance was

where

$$R=4nM,$$

R=the resistance of the standard resistor in absolute ohms,
M=the computed mutual inductance of the standard in absolute henrys, and
n=the number of reversals of current in the secondary per second.

The resistance in international ohms of the standard resistor was obtained by direct comparison with the fundamental standards of the National Bureau of Standards.

The primary of the standard mutual inductor was a long helix from which two sections were removed. The porcelain cylindrical form for this helix was 83 cm long, 41 cm in diameter, and had a wall thickness of 6 cm. A screw thread having a pitch of 2 mm was ground and lapped in the outer surface. It was wound with wire 1.7 mm in diameter. The two portions that were removed were each 5.6 cm long and started 2.5 cm from the median plane.

The secondary was wound on a form made by cementing together three glass disks, the two outer ones having larger diameters than the inner one. The cemented structure formed a ring having a channel 8 mm wide and 25 mm deep. The mean diameter of the secondary was 52.5 cm. The median plane of the secondary coincided with the median plane of the primary.

The important dimensions for computing the inductance were the diameter and the pitch of the helix. The maximum variations in diameter were less than 20 ppm. The variations in pitch were negligibly small. The mean pitch was measured to about 10 ppm. The error in the computed inductance was probably less than 10 ppm.

The electrical measurements repeated to 1 or 2 ppm. However, there was the possibility of systematic errors, as very little variation of conditions was introduced.

This investigation suffers only by the fact that it has not been subjected to the critical analysis that is inherent in preparing a report for publication. If published reports only are considered, the result of this investigation is preliminary and should be given zero weight. However, the author of this review, knowing the reasons for the delay in publication, feels justified in giving it an intermediate weight.

III. VALUES OF THE ABSOLUTE OHM IN TERMS OF THE MEAN INTERNATIONAL OHM

The results of all the determinations discussed in this review are given in table 1. Each result has been expressed in terms of that value of the mean international ohm which had been established nearest in time to the determination. The results of Yoneda and Zickner have been given zero weight, as both the authors state that they are preliminary and no additional evidence is available. In Vigoureux's work, there were uncertainties in the electrical measurements and variations in the mechanical dimensions of the apparatus so that a weight of unity was assigned. The same weight was given to the results of Jouaust, Picard, and Hérou, who used novel methods of measuring the mechanical dimensions and of making the electrical measurements, and who did not use sufficient checks to convince the reader that systematic errors were eliminated. The 1936 result of Curtis, Moon, and Sparks has been given a weight of two because of the thorough checking that was employed. The only weakness of this work was the inherent imperfections in the helices. The work of Wenner, Thomas, Cooter, and Kotter, although carried out with great care, may still contain some systematic errors that will be brought to light when it is prepared for publication. It has therefore been given a weight of three. The results of Hartshorn and Astbury and of Curtis, Moon, and Sparks in 1938 are each given a weight of five. The inductor of Hartshorn and Astbury was less perfect than the one of Curtis, Moon, and Sparks, but the electrical measurements of the former showed smaller variations than those of the latter. These two researches appear to have eliminated sources of error more completely than any of the others and hence are given the highest weight.

TABLE 1.—*Results of recent determinations of the absolute ohm*

Year	Author	Value of 1 mean international ohm in absolute ohms	Assigned weight
1936	Curtis, Moon, and Sparks	1.000 454	2
1937	Vigoureux	1.000 499	1
1937	Yoneda	1.000 465	.....
1937	Hartshorn and Astbury	1.000 505	5
1938	Jouaust, Picard, and Hérou	1.000 520	2
1938	Curtis, Moon, and Sparks	1.000 482	5
1939	Zickner	1.000 50	.....
1939	Wenner, Thomas, Cooter, and Kotter	1.000 488	3
	Weighted mean	**1.000 490**	.....

The results given in table 1 indicate that the most probable value of the absolute ohm is

1 mean international ohm = 1.000 490 absolute ohms.

Although the weighting has been made according to the best judgment of the author, actually the method of weighting affects the result but little. The means obtained by various methods of weighting the results are given in table 2.

TABLE 2.—*Weighted means obtained by various methods of weighting the eight results on the absolute ohm*

Method of weighting	Resulting weighted mean	Weighted mean deviation from the mean
		ppm [1]
Weighted as in table 1	1.000 490	14
Equal weight to all eight	1.000 489	17
Equal weight to 6 not preliminary	1.000 491	17
Equal weight to 3 with highest weights	1.000 492	9

[1] The mean value from which the deviations are taken is the corresponding value in the preceding column. The weighting is that indicated in the first column for that row.

IV. VALUES OF THE ABSOLUTE OHM IN CERTIFIED INTERNATIONAL OHMS

In certifying standard resistors, each of the national laboratories has used a value of an international ohm that is different from the mean international ohm. In fact, some laboratories do not use the same unit of resistance in their regular certifications as in their reports to the International Bureau, although both units may be called international ohms. Hence a laboratory which maintains its resistance unit by means of standards certified by a national laboratory must know the relationship between the mean international ohm and the unit used in certifying resistors before conversion to absolute ohms can be effected. The necessity will be illustrated by explaining the different units of resistance that are now used at the National Bureau of Standards, giving enough historical background for the reader to appreciate the way in which these units arose.

The international ohm as now certified by the National Bureau of Standards has been maintained, without intentional change, for 35 years by means of standard resistors. A value of resistance based on the mercury ohm was assigned to each of a group of standard resistors in 1908. The unit based on the values of these standard resistors has been used by the Bureau in regular certification of standards since that time and is herein called the "international ohm (certified NBS)."

In 1910 an International Technical Committee met at the National Bureau of Standards to determine the value of the international volt from measurements with silver voltameters. Before proceeding with the determination of the volt, the Committee had to reach an agreement concerning the most probable value of the international ohm. They agreed to use the average of the two latest determinations of the mercury ohm up to that time. This unit was only 7 ppm smaller than the unit which was then in use at the National Bureau of Standards. At that time it did not seem worth while to change the values assigned to the Bureau's standards by this small amount, so that the ohm as used before 1910 has continued to be the basis of certified values up to the present time. However, when international cooperation was again undertaken after some 20 years, this difference of 7 ppm was of some moment. In the international comparisons made during the last 10 years a unit has been used in which a correction for the difference of 7 ppm has been made. The published

results of the Bureau's absolute electrical measurements have been made in terms of this unit, which has been referred to as the "NBS international ohm." The value of a resistance in international ohms (certified NBS) may be converted to its value in NBS international ohms by multiplying by 1.000 007.

The comparisons of the units of resistance made at the International Bureau of Weights and Measures in 1939 gave the NBS international ohm as 3.2 parts per million less than the mean international ohm, or

1 mean international ohm=1.000 003 NBS international ohms.

Hence

1 international ohm (certified NBS)=1.000 004 mean int. ohms.

It follows from the results given in table 1 that

1 international ohm (certified NBS)=1.000 494 absolute ohms.

V. RÉSUMÉ OF ABSOLUTE-AMPERE DETERMINATIONS

Seven different researches on the value of the absolute ampere have been reported during the last decade. The following analysis covers all of them. In all the determinations, the value in absolute amperes of a current was obtained by comparing the electromagnetic force on a conductor carrying a current with the gravitational force on a known mass, and the value in international amperes of the same current was obtained by observing the fall of potential which it produced in a standard resistor.

(a) 1934: CURTIS AND CURTIS AT NBS [10]

The Rayleigh current balance used by Rosa, Dorsey, and Miller [11] in 1912 was reassembled and used in this investigation. In this balance the electromagnetic force is exerted between a multilayer moving coil and two multilayer fixed coils of larger diameter, all of which carry the same current. The moving coil, with its axis vertical, is suspended from the pan of a balance; the fixed coils are mounted one above, the other below the moving coil. The electromagnetic force is balanced by the gravitational force on a mass placed on the pan of the balance to which the moving coil is attached.

Several sets of coils were employed, all of which were made by winding round wire in a channel cut in a brass form. The moving coils had diameters of either 20 or 25 cm, and the fixed coils had diameters of 40 or 50 cm. Each coil had an approximately square cross section, a side of which did not exceed one-twentieth of the mean diameter of the coil.

By experimentally adjusting the axial distance between the moving coil and each fixed coil until, with a given current, the force between the coils was a maximum, the method of computing the current was so simplified that, for a first approximation, the only mechanical quantity required was the ratio of the mean radii of the coils. This was obtained by comparing the currents required to produce equal and opposite magnetic fields at their centers when the coils were coaxial and concentric. Hence no precise mechanical measurement of the

[10] H. L. Curtis and R. W. Curtis, *An absolute determination of the ampere*, BS J. Research **12**, 665 (1934) RP685.

[11] E. B. Rosa, N. E. Dorsey, and J. M. Miller, *A determination of the international ampere in absolute measure*, Bul. BS **8**, 269 (1912) S171.

diameter was required. The next approximation was developed by assuming that the current was uniformly distributed over the cross section. Then the computation of the absolute value of the current required in addition to the ratio of the mean radii, the ratios of both the width and depth of each coil to its diameter. These additional ratios were determined by Rosa, Dorsey, and Miller when the coils were constructed by making measurements of each dimension.

In the reassembly, slight changes were made to improve the convenience of operation, but the same wire-wound coils of many layers were employed. The ratios of the radii of the coils were redetermined, but no checks on the additional ratios were possible.

The results indicate that the value obtained with a set of coils, each of which had small ratios of the width and the depth of the cross section to the diameter of the coil, was more dependable than the value obtained when this ratio was larger. However, it appears that the correction for the cross sections of the coils could not in any case be accurately made, as the wires were not uniformly distributed throughout the cross section. In winding the coils, the wire could not be uniformly distributed, this being especially the case where the wire passed from one layer to the next. The coils used in this investigation are so inferior to those used in more recent investigation that the result has been given zero weight.

(b) 1935: DUPOUY AND JOUAUST AT LCE [13]

The authors used a balance of the type proposed by Cotton. In this type of balance, the electromagnetic force between a short conductor carrying a current and a strong magnetic field in which it is placed, is compared with a gravitational force. The computation of the current requires a knowledge of the magnetic induction in the region occupied by the conductor. As there is no independent method of measuring this induction with precision, the absolute value of the current is not accurately determined. The authors state that their result may be in error by a few parts in 10,000. The result has been given zero weight.

(c) 1936: VIGOUREUX AT NPL [13]

This author used the balance designed by Ayrton, Mather, and Smith, but constructed new coils for it.[14] The coils were in the form of helices of wire, wound in screw threads cut in marble cylinders on a lathe. Two moving coils and four fixed coils were employed. One moving coil was hung on each of the pans of a balance. These moving coils were cylinders 20 cm in diameter having a length of winding of 15.2 cm. The two fixed coils, which were used in conjunction with a single moving coil, were wound near the two ends of a hollow cylinder of marble about 32 cm in diameter. Each helix was 11 cm long, and there was a 3-cm gap between them. Each pair of fixed coils was coaxial with its moving coil, and the center of the gap between the fixed coils coincided with the center of the moving coil.

[13] G. Dupouy and R. Jouaust, *On the absolute measurement of a magnetic field and the determination of the ampere in absolute value*, J. phys. et radium [7] **6**, 123 (1935).

[13] P. Vigoureux, *An absolute determination of the ampere*, Trans. Roy. Soc. (London) [A] **236**, 133 (1936); Nat. Phys. Lab. Collected Researches **24**, 173 (1938).

[14] W. E. Ayrton, T. Mather, and F. E. Smith, *A new current weigher and a determination of the electromotive force of the normal Weston cadmium cell*, Trans. Roy. Soc. (London) [A] **207**, 463 (1908); Nat. Phys. Lab. Collected Researches **4**, 1 (1908).

In deriving the formula for computing the current, a first approximation was obtained by assuming that each coil was a current sheet. Corrections were then applied for the discrete windings of the coils and for the interaction between the two sets of coils.

The helices showed rather large variations in their dimensions. The maximum variation in diameter of each fixed coil was 50 ppm and of each moving coil 100 ppm. All the coils had periodic variations in pitch, the total amplitude being about 10μ, in a pitch of 1,000 μ. The author states, "This periodic error constitutes a serious defect in the coils of this current balance."

The result is given as the electromotive force of the neutral cadmium cell at 20° C. The voltage of the typical cell as realized at the NPL was found to be 1.01816 abs amp $\times$ NPL int. ohm. Some later measurements gave 1.018151. The author states that, neglecting a possible error in the value of gravity at Potsdam, the "accuracy will be assessed" at 20 ppm. In view of the variations in the mechanical dimensions noted above, it seems that a systematic error of more than 20 ppm might be present.

Several steps are required to convert the value given by the author from the units which he used to those herein employed. The result obtained by making this conversion is given in table 3. Because the dimensions of the coils showed large variations, the result is given an intermediate weight.

(d) 1937: YONEDA AND ISHIBASHI AT ETL [15]

The authors used a Rayleigh current balance with wire-wound coils. The apparatus was very similar to that employed by Curtis and Curtis in 1934. No details of the apparatus or of the methods of measurement are available. Only a preliminary result is given. Zero weight is assigned to the result.

(e) 1939: CURTIS, CURTIS, AND CRITCHFIELD AT NBS [16]

This investigation is a continuation of the work of Curtis and Curtis. Two new fixed coils and two new moving coils were used in the Rayleigh current balance, but otherwise the same apparatus was used and the same technique followed as that described in the first review of this series. Both of the new fixed coils and one moving coil were flat spirals of aluminum ribbon. The second moving coil was a short helix. The insulation of the aluminum ribbon consisted of a thin layer of aluminum oxide, which was formed by electrolytic action on the surface of the ribbon. The coils were very compact and uniform. They conformed much more closely to the requirements assumed in the mathematical derivation of the formula for computing the absolute value of the current than was the case with the multiple-layer coils of wire.

The short helix used as a second moving coil consisted of wire wound in a screw thread that was lapped in a glass form. The length of the winding was 2.6 cm. The formula for computing the current when using this moving coil was a modification of the formula for coils with an approximately square cross section. The diameter was not meas-

[15] R. Yoneda and Y. Ishibashi, *Absolute determination of current*, Procès-verbaux, Comité International des Poids et Mesures [2] **18**, 185 (1937).

[16] H. L. Curtis, R. W. Curtis, and C. L. Critchfield, *An absolute determination of the ampere, using improved coils*, J. Research NBS **23**, 485 (1939) RP1200.

red for this research, as the ratio of its diameter to that of each of he fixed coils was measured by the magnetic method.

The most probable value of the absolute ampere as reported by the uthors was an average of four values, two obtained when using the oils described in the preceding paragraphs and two from the paper of Curtis and Curtis. It now seems desirable to discard all results obained with multiple-layer coils of wire such as were used by Curtis nd Curtis. Hence the result for this research given in the table which follows is the average of the two values obtained when using piral fixed coils with two different moving coils, one being a spiral nd the other a short helix. It is slightly different from the results iven in the paper as the most probable value of the absolute ampere. A high weight is assigned to the result.

(f) 1939: VON STEINWEHR AT PTR [17]

A Rayleigh current balance was used in this investigation. Methods of computation and operation similar to those used by Curtis and Curtis were employed. Most of his coils were wound with ribbon. A pair of fixed coils and a moving coil were made by winding a spiral of copper ribbon in which the turns were insulated by a layer of silk. Two moving coils were made from aluminum ribbon, insulating the turns by a layer of aluminum oxide as described by Curtis, Curtis, and Critchfield. One pair of fixed coils was wound with enamel-covered wire. The author states: "The results . . . must not yet be considered final." Zero weight is assigned to the result.

(g) 1942: CURTIS, DRISCOLL, AND CRITCHFIELD AT NBS [18]

In this investigation the apparatus was the same as that described in the fifth review, except that the fixed coils of aluminum ribbon were replaced by helices which were the two halves of a single helix electrically divided into two parts by attaching a lead at the midpoint of the winding. The method of obtaining the constants of the balance was quite different from that employed when the fixed coils of aluminum ribbon were used, because with the helical fixed coils the magnetic method of obtaining the ratio of radii of fixed and moving coils was not applicable. When the helical moving coil was used, the force per unit current was computed from the dimensions of the fixed and moving helices. When the spiral moving coil of aluminum ribbon was used, its effective radius was obtained by an indirect method.

When the helical moving coil was employed, the balance was similar to the one used by Vigoureux at the NPL, the principal difference being that the moving coil was much shorter.

The variations in the dimensions of the helices were small. The maximum variation in outside diameter of the fixed helix having a diameter of 46 cm was 0.4 μ, or 1 ppm. The length of the two halves, each 14 cm long, did not differ by more than 0.8 μ, indicating very uniform pitch. No periodic error in the pitch could be detected. The

[17] H. von Steinwehr, *Report concerning the progress of the experiments on a determination of the international ampere in absolute units*, Procès-verbaux Comité Consultatif d'Electricité, p. E51, 1939 (advance print for Procès-verbaux, Comité International des Poids et Mesures).

[18] R. W. Curtis, R. L. Driscoll, and C. L. Critchfield, *An absolute determination of the ampere, using helical and spiral coils*, J. Research NBS **28**, 133 (1942) RP1449.

outer surface of the moving coil with the helical winding had the shape of an elliptical cylinder with a mean diameter of 24.5 cm and a length of 2.6 cm. The difference between the major and minor diameters was 13 μ. However, the average diameter as obtained from measurements at six equally spaced generators differed from that obtained from the six interspaced generators by only 0.1 μ, or less than 1 part in a million. The pitch was so uniform that no variation exceeding 0.1 μ could be detected.

The mean diameter of the spiral moving coil was obtained by an indirect comparison with the helical moving coil. The ratio of the diameter of each moving coil to the diameter of each of six fixed coils was obtained by a magnetic method. The mean deviation in the six ratios of the diameters of the two moving coils was 5 ppm.

The authors include in their final value the results of the investigation that was completed in 1939, as well as those obtained with the coils described in the preceding paragraphs. However, the value for the 1942 investigation as given in table 3 is the average of only the two values obtained with the subdivided helix for the fixed coils and with either a spiral or a short helix as the moving coil. A high weight is given to this result.

VI. VALUES OF THE ABSOLUTE AMPERE

The results of all determinations of the absolute ampere herein discussed are given in table 3. Weights have been arbitrarily assigned to the result of each determination.

TABLE 3.—*Results of recent determinations of the absolute ampere*

Year	Author	Value of 1 mean international ampere in absolute amperes	Assigned weight
1934	Curtis and Curtis	0.999 934	
1935	Dupouy and Jouaust	.999 8₀	
1936	Vigoureux	.999 863	3
1937	Yoneda and Ishibashi	.999 938	
1939	Curtis, Curtis, and Critchfield	.999 860	3
1939	Von Steinwehr	1.000 04	
1942	Curtis, Driscoll, and Critchfield	0.999 856	3
	Weighted mean	*0.999 859	

* This value is corrected on page 252 for the new value of the acceleration of gravity.

The weighting markedly affects the results. This is shown by the values given in table 4. This is in contrast with the results for the ohm, as shown in table 2.

TABLE 4.—*Weighted means obtained by various methods of weighting the seven results on the absolute ampere*

Method of weighting	Resulting weighted mean	Weighted mean deviation from the mean
		ppm [1]
Weighted as in table 3	0.999 850	3
Equal weight to all seven	.999 912	51
Equal weight to 4 not preliminary	.999 878	28
Equal weight to 3 with highest weights	.999 860	2

[1] The mean value from which the deviations are taken is the corresponding value in the preceding column. The weighting is that indicated in the first column of the corresponding line.

The results of Curtis and Curtis and of Yoneda and Ishibashi, both of which were obtained with multilayer coils of round wire, have been given zero weight. The result of Dupouy and Jouaust was incidental to another investigation, and the authors do not claim an accuracy of much more than 1 part in 10,000, so it also has been given a zero weight. The result of Von Steinwehr is given by the author as preliminary, and the wide variation of his results when using different coils supplies an added reason for giving zero weight. The weight for the result of Vigoureux is not the highest because of the imperfections of the coils in his balance. Only two determinations can be given the highest weight, and both of these are from the laboratories of the National Bureau of Standards.

The value of the acceleration of gravity, which enters into all seven results, was in every case based on that obtained at Potsdam, Germany, by an absolute measurement carried out during the first decade of this century. Transfers by pendulums of invariable length have been made from Potsdam to the laboratories making the absolute measurement of current. In the last few years two absolute determinations of the value of gravity have been made, one at the NPL and the other at the NBS. Moreover, the methods used in reducing the data of the Potsdam determination have been reexamined.[19] The revised Potsdam value was compared with the two more recent determinations. The conclusion was reached that the most probable value of the acceleration of gravity at the gravity station of the National Bureau of Standards is

$$980.083 \text{ cm/sec}^2.$$

At the pan of the current balance, the value becomes

$$980.082 \text{ cm/sec}^2.$$

The value of gravity used in the three recent determinations of the absolute ampere at the NBS was

$$980.095 \text{ cm/sec}^2.$$

This difference of 13 ppm in the numerical value of the acceleration

[19] H. L. Dryden, *A reexamination of the Potsdam absolute determination of gravity*, J. Research NBS **29**, 303 (1942) RP1502.

of gravity makes a decrease in value of the absolute ampere of 6.5 ppm. Presumably, the value of the absolute ampere obtained at other laboratories requires an identical correction. Making this correction to the weighted mean value obtained from table 3,

1 mean international ampere=0.999 853 absolute ampere

From relationships given elsewhere between the mean international ohm and volt and the international ohm and volt as certified by the National Bureau of Standards, it follows that

1 international ampere (certified NBS)=0.999 838 absolute ampere.

VII. MAINTENANCE OF THE VOLT AND ITS ABSOLUTE VALUE

The volt is maintained at the national standardizing laboratories by groups of standard cells.[20] The group at the National Bureau of Standards consists of about 20 cells, several of which were made in 1906. In 1911 the average of the group was assigned a value in international volts that was determined from the international ohm as obtained from a column of mercury, and the international ampere as obtained from deposits of silver in a silver voltameter. The unit thus established has been maintained until the present time and has been used both in international comparisons and in certifications. Comparisons made at the International Bureau in 1939 showed that this unit of electromotive force is 11 ppm less than the mean international unit. From the weighted mean values of the absolute ohm and ampere in terms of the mean international ohm and ampere, it follows that

1 mean international volt=1.000 343 absolute volts.

Hence

1 international volt (certified NBS)=1.000 332 absolute volts.

VIII. THE UNITS OF INDUCTANCE AND CAPACITANCE

The units of inductance and capacitance are maintained at each of two of the national laboratories by reference to a standard inductor whose inductance can be computed from its mechanical dimensions. In two other national laboratories, the units are not maintained independent of the other electrical units but standards of inductance and capacitance are frequently measured in terms of resistance and time. The latter method is employed at the National Bureau of Standards.

[20] For methods used by the different national laboratories to maintain the units of resistance and of electromotive force, see H. L. Curtis, The Establishment and Maintenance of the Electrical Units, Bul. Nat. Research Council No. 93 (1933). So far as the author knows, the only change in methods which has been adopted since the above was written is the use of improved standard resistors at the National Bureau of Standards.

Measurements of time can be made with extreme accuracy. Hence the relationships between the various units of inductance are identical with those of the units of resistance, but between the units of capacitance the relationships are the reciprocals of those of the units of resistance.

Hence

1 international henry (certified NBS) = 1.000 007 NBS international henrys.
= 1.000 004 mean international henrys.
= 1.000 494 absolute henrys.

Also

1 international farad (certified NBS) = 0.999 993 NBS international farad.
= 0.999 996 mean international farad.
= 0.999 506 absolute farad.

IX. SUMMARY

The factors for converting the value of a standard as certified in international units by the National Bureau of Standards to its value in absolute units according to the analysis of this paper are given in table 5.

TABLE 5.—*Factors for converting the value of a standard in international electrical units (certified NBS) to its value in absolute units*

Quantity	Unit	Conversion factor [1]
Resistance	Ohm	1.000 494
Electromotive force	Volt	1.000 332
Current	Ampere	0.999 838
Quantity	Coulomb	.999 838
Inductance	Henry	1.000 494
Capacitance	Farad	0.999 506
Energy	Joule	1.000 170
Power	Watt	1.000 170

[1] The figures in the last decimal place have little significance.

X. COMPARISONS OF RESULTS WITH THOSE OF OTHER RECENT COMPILATIONS

Two other compilations of the absolute values of the electrical units have recently been made. The values of the ohm and ampere as given by the three compilers are collected in table 6. Dunnington [21] gave the relation of the NBS international ohm and ampere to the absolute ohm and ampere but did not indicate the analysis by which he arrived at

[21] F. G. Dunnington, *The atomic constants: A revaluation and an analysis of the discrepancy*, Rev. Modern Phys. 11, 65 (1939).

the published results. For this compilation his values have been reduced to mean international ohms and amperes and his value of the ampere changed to correspond to the recent determinations of gravity. Stille [22] made a complete and impartial analysis of the recent determinations of the ohm and the ampere. He has modified the results as published by the different authors, so that all are expressed as the value in absolute units of 1 mean international unit. His final value for the ampere is carried only to 1 part in a hundred thousand, but he has given several possible interpretations in which the value is carried to 1 part in a million. The value which he appears to favor, corrected to correspond to the value of gravity used in this compilation, has been chosen for inclusion in table 6.

TABLE 6.—*Conversion factors given by various compilers*

Compiler	Value in absolute units of 1 mean international unit	
	Ohm	Ampere
Dunnington	1.000 488	0.999 972
Stille	1.000 493	.999 880
Curtis	1.000 490	.999 853

The value of the ohm seems to be well established, since the maximum difference between different compilers is 3 ppm. The value of the ampere is not so well established as there is a maximum difference of 119 parts in a million. This large difference can be explained by the following considerations. Dunnington did not have available one, and probably two, of the recent determinations of the National Bureau of Standards. Probably he would now give a value lower than the one he used in 1939. Stille did not have available the paper by Curtis, Driscoll, and Critchfield, which would have lowered his average. However, the difference is largely due to the adoption by the writer in this compilation of a system of weighting results. Stille has done the equivalent of this by giving for one author several values corresponding to the different sets of coils he used, whereas for others he gave only the average of two or more sets of coils. The weighing in this paper is of necessity arbitrary, but it represents the best judgment of the author of this review.

WASHINGTON, May 15, 1944.

[22] U. Stille, *The conversion factors from the international to the absolute electrical units*, Z. Physik. 121, 34 (1943).

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1607

Part of Journal of Research of the National Bureau of Standards, Volume 33, October 1944

HEATS OF COMBUSTION OF EIGHT NORMAL PARAFFIN HYDROCARBONS IN THE LIQUID STATE

By Edward J. Prosen and Frederick D. Rossini

ABSTRACT

The heats of combustion of *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-dodecane, and *n*-hexadecane, in the liquid state, were measured with a bomb calorimeter. The samples of hydrocarbon were of known high purity, were inclosed in thin glass bulbs and placed in a platinum cup in the calorimetric bomb with purified oxygen at a pressure of 30 atm, and were ignited electrically with a wire fuse. The amount of reaction in each experiment was determined from the amount of carbon dioxide formed by the combustion. Tests were made for the presence of carbon monoxide and other products of incomplete combustion. The calorimeter system was calibrated with electrical energy.

From the experimental data were calculated the following values for the heat of combustion, at 25° C and constant pressure, of the liquid hydrocarbon in gaseous oxygen to form gaseous carbon dioxide and liquid water, with all the reactants and products in their thermodynamic standard reference states, in int. kj/mole: *n*-pentane, 3508.56 ±0.77; *n*-hexane, 4162.34 ±0.83; *n*-heptane, 4816.35 ±0.87; *n*-octane, 5469.82 ±1.05; *n*-nonane, 6123.90 ±1.12; *n*-decane, 6777.47 ±1.52; *n*-dodecane, 8085.20 ±1.65; *n*-hexadecane, 10699.1 ±2.8. The corresponding values in kcal/mole, obtained by using the factor 1/4.1833, are *n*-pentane, 838.71 ±0.18; *n*-hexane, 994.99 ±0.20; *n*-heptane, 1151.33 ±0.21 *n*-octane, 1307.54 ±0.25; *n*-nonane, 1463.89 ±0.27; *n*-decane, 1620.13 ±0.36; *n*-dodecane, 1932.73 ±0.39; *n*-hexadecane, 2557.58 ±0.68.

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I. INTRODUCTION

In continuation of the work of the thermochemical laboratory of this Bureau in determining the thermochemical constants of substances, the heats of combustion of *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-dodecane, and *n*-hexadecane, in the liquid state, were measured. This paper describes in detail the calorimetric and chemical apparatus and procedure and gives the experimental data obtained.

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, ETC.

The unit of energy upon which the experimental values of this investigation are based is the international joule determined by the standards of resistance (international ohms), electromotive force (international volts), and time (mean solar seconds) maintained at this Bureau.

For the conversion of values in international joules to values expressed in terms of the conventional thermochemical calorie, the following relation is used [1] :[1]

4.1833 international joules (NBS)=1 calorie.

The molecular weight of carbon dioxide, the mass of which was used to determine the amount of reaction, was taken as 44.010, from the 1941 table of International Atomic Weights [2].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [3]. In other cases, reasonable estimates of the uncertainty were made.

III. METHOD

The method is the substitution method, in which the heat evolved by a measured amount of chemical reaction is compared with the heat evolved by a measured amount of electrical energy, with the calorimeter system serving as the absorber and comparator of the two kinds of energy. A standard calorimeter system was used and the temperature rise was made substantially the same in all experiments.

The energy equivalent of the calorimeter is determined in a series of experiments with electrical energy. The relation used in computing the energy equivalent of the calorimeter E_v, is

$$E_v = fY/\Delta R_v,$$

where Y is the observed electrical energy; f is a constant whose value is the resultant of the various calibration factors associated with the instruments used in measuring the electrical energy, such as the stand-

[1] Figures in brackets indicate the literature references at the end of this paper.

ard resistances, standard cell, resistance coils of the potentiometer, timing apparatus, etc., and ΔR_y is the rise in temperature measured as an increase in resistance in ohms of the given platinum resistance thermometer at the given mean temperature. The product fY gives the electrical energy in terms of the unit fixed by the units of resistance, electromotive force, and time. In the present experiments this unit is the international joule.

The amount of chemical reaction that produces, in the calorimeter, a rise in temperature substantially equal to that in the experiments with electrical energy is determined in a series of calorimetric reaction experiments. The relation used in reducing the data of these experiments is

$$B' = B/g = \Delta R_w/Wg,$$

where W is the observed mass of the substance (in the present experiments, carbon dioxide) that is used to determine the amount of reaction, g is a factor whose value is the resultant of the various factors required to convert the observed mass of the carbon dioxide to the number of moles of the desired pure reaction ΔR_w is the rise in temperature measured as an increase in resistance in ohms of the given platinum resistance thermometer at the given mean temperature, and B is a constant representing the temperature (expressed in ohms) per unit mass of the selected substance, carbon dioxide, that determines the amount of reaction.

The experimental value of the heat evolved per mole of the reaction being studied is

$$Q = E_c B' = (Y/\Delta R_y)(\Delta R_w/W)(f/g).$$

The ratios $Y/\Delta R_y$ and $\Delta R_w/W$ are evaluated in the electrical energy experiments and the chemical reaction experiments, respectively, and the ratio f/g includes all the constant factors involved in the reduction of the data.

In the present investigation, the over-all uncertainty assigned to any final value Q was taken as the combination (square root of the sum of the squares) of an uncertainty of 0.010 percent in f, 0.010 percent in g, twice the standard deviation of the mean of the series of experiments made to evaluate $Y/\Delta R_y$, and twice the standard deviation of the mean of the series of experiments made to evaluate $\Delta R_w/W$.

IV. MATERIALS, CHEMICAL APPARATUS, AND PROCEDURE

1. SOURCE AND PURITY OF THE HYDROCARBONS

n-Pentane.—The material used in series I and II and in two experiments of series III was from some purified material prepared by the American Petroleum Institute Research Project 6 at this Bureau for the determination of physical properties and was found by A. R. Glasgow, Jr., from time-temperature freezing and melting curves [12], to have 0.0014 ± 0.0007 mole fraction of impurity. The material used in two other experiments of series III was from the lot synthesized by Mair [13]. From the value of the freezing point reported by him, and the

value for *n*-pentane of zero impurity [12], the amount of impurity in the latter sample was estimated to be less than 0.0010 mole fraction.

n-Hexane.—The material used in the experiments of series I and series III is the same as lot I, and for the experiments of series II the same as lot II, described in the authors' report on the isomeric hexanes [4]. From the value of the freezing point reported by Mair [13], and the value for *n*-hexane for zero impurity [12], the amount of impurity in the *n*-hexane used in experiments of series II was estimated to be 0.0010 ± 0.0006 mole fraction.

n-Heptane.—The material used in the experiments of series I and II was the same as that described in the report on the isomeric heptanes [15]. The amount of impurity in the *n*-heptane used in the experiments of series III was determined by A. R. Glasgow, Jr., from time-temperature freezing and melting curves [12] to be 0.0012 ± 0.0006 mole fraction. This material was purified by the API Research Project 6 at this Bureau for the determination of physical properties.

n-Octane.—The lot of material used in the experiments of series I and that used in the experiments of series II were from material synthesized by the API Hydrocarbon Research Project at the Ohio State University.[2] These two lots of *n*-octane were found by A. R. Glasgow, Jr., from freezing-point measurements, to have, respectively, 0.0080 ± 0.0010 and 0.0035 ± 0.0005 mole fraction of impurity.

n-Nonane and n-decane.—These materials were from the lots synthesized by Mair [13]. From the values of the freezing points reported by him, and the values for *n*-nonane and *n*-decane of zero impurity [12], the amounts of impurity in these samples were estimated to be 0.007 ± 0.002 and 0.0006 ± 0.0004 mole fraction, respectively.

n-Dodecane.—This material was from the best lot isolated from petroleum by Mair and Streiff [14], who reported the amount of impurity to be less than 0.0006 mole fraction.

n-Hexadecane.—This material was purified by crystallization and adsorption by A. J. Streiff and B. J. Mair from material supplied by the E. I. du Pont de Nemours Co.[3] From the value of the freezing point, determined by A. R. Glasgow, Jr., the amount of impurity in this sample was determined to be 0.040 ± 0.004 mole fraction. From the manner of purification, it would be expected that the impurities in the *n*-hexadecane would be pentadecanes, hexadecanes, and heptadecanes. With the amount of reaction being determined from the mass of carbon dioxide formed in the combustion, it can be calculated that this apparently large amount of impurity in the *n*-hexadecane would not affect the heat of combustion by more than 1 or 2 parts in 10,000. On account of this impurity, an additional uncertainty of 0.02 percent is carried into the over-all uncertainty assigned to the value of the heat of combustion for *n*-hexadecane.

The amounts of impurity in the samples of *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, and *n*-dodecane are such that they would affect the value of the heat of combustion by less than 5 parts in 100,000. This conclusion is based on the fact that the manner of preparation and purification of these compounds was

[2] These materials were made available by C. E. Boord, supervisor of that project, and George Calingaert, chairman of the Subcommittee on Physical Properties.
[3] This material was made available by Don M. Smith.

such that the small amounts of impurities remaining would be largely isomeric.

2. SEALING OF THE HYDROCARBONS IN GLASS AMPOULES

The hydrocarbons were sealed in glass ampoules, prior to combustion in the bomb, in the manner described in detail in the previous report [4].

3. PURIFICATION OF THE OXYGEN USED FOR COMBUSTION

The oxygen used for the combustion of the hydrocarbons was ordinary commercial oxygen, which was freed of combustible impurities by passage through hot copper oxide, using the apparatus and procedure previously described for this purpose [4].

4. EXAMINATION OF THE PRODUCTS OF COMBUSTION

The products of combustion were examined to determine the amount of carbon dioxide formed in the main reaction of combustion in the bomb, the amount of nitric acid formed by oxidation of some of the nitrogen in the oxygen used for combustion, and the amount of carbon dioxide formed by subsequent oxidation of any products of incomplete combustion. In only one experiment (on *n*-octane) was there found any evidence of incomplete combustion. The apparatus and procedure previously described [4] were used.

5. DETERMINATION OF THE AMOUNT OF REACTION

For each calorimetric combustion experiment, the amount of reaction was determined from the mass of carbon dioxide formed, taking 1 mole (44.010 g) of carbon dioxide as equal to $1/n$ moles of the given hydrocarbon, n being the number of carbon atoms per molecule. The same apparatus and procedure were used as before, except that, in the later experiments, a new form of absorption tube was used, as described below.

6. ABSORPTION TUBES FOR WEIGHING

The new absorption tube [4] used in the latter part of this investigation is shown in figure 1. The gas enters at the left, passes downward through the body of the tube, which contains, in order, Ascarite, anhydrous magnesium perchlorate, and phosphorus pentoxide, separated by layers of dry, shredded asbestos. The gas leaves the body of the tube at the bottom, passes upward through the side tube, reenters and passes through the cap through a right-angle tube and leaves at the right. The tube is closed by turning the cap one-eighth turn in either direction. The advantages of this tube over the conventional U-tube for this type of work are (a) greater compactness, (b) greater ease in lining up two tubes in series in an analytical train, and (c) presence of only one lubricated ground joint. As used in this investigation in the manner described above, the new tube had the disadvantage that it was more difficult to clean after being used to

[4] See also reference [11].

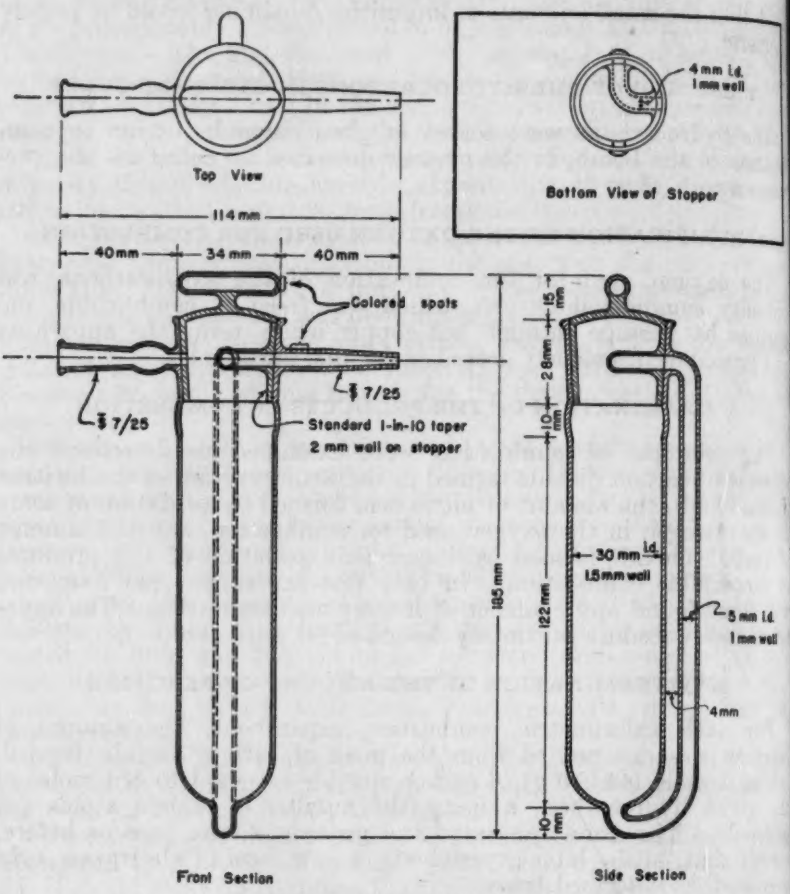

FIGURE 1.—*Absorption tube.*
(See text for explanation.)

absorb carbon dioxide. The Ascarite becomes hard after such absorption, and when it was placed at the top of the tube, it was necessary to dig a hole through it to remove the loose phosphorus pentoxide and magnesium perchlorate before the Ascarite is dissolved away with water. This one disadvantage has subsequently been eliminated by placing the absorbents in the absorption tube in the reverse order and passing the gas through in the opposite direction.

V. CALORIMETRIC APPARATUS

1. CALORIMETER ASSEMBLY

The calorimeter system was the same as that used in the previous investigation [4]. Some minor changes in the physical part of the system were made during the course of the investigation, which resulted in four slightly different calorimeter systems, A, B_1, B_2, and C, with the energy equivalents of systems B_1 and B_2 being substan-

tially identical. (See section VII–1 of this paper.) The calorimeter heater used in the experiments with system B_2 and system C was the one described on page 293 of reference [4] and was tightly fitting on the bomb body. The calorimeter heater used in the experiments with system A and with system B_1 was of the same design as the foregoing, except that the diameter of the cylinder was 9.0 cm instead of 7.8 cm, and the heater fitted loosely on the bomb body.

The rate of stirring of the calorimeter was 285 rpm in all the experiments with system A and system B_1 and was 350 rpm in all the remaining experiments, except where stated differently in table 1.

2. COMBUSTION BOMB

The combustion bomb described in reference [4] was used in all the experiments except those with the calorimeter system A, in which a bronze sleeve with 10 steel setscrews was used instead of the stainless-steel sleeve with 16 setscrews shown as C in figure 1 on page 294 of reference [4]. The stainless-steel sleeve was found to be superior from the standpoint of providing more easily a tight closure of the bomb head on the body. Leakage of gas from the bomb at the time of explosion was tested for in a number of experiments throughout the investigation.

3. POWER-MEASURING APPARATUS

The electrical power was computed as the product of the potential drop per ohm across a 0.1-ohm standard resistor in series with the calorimeter heater and the potential drop across the calorimeter heater, corrected for the current through the standard resistors in parallel with the calorimeter heater. The potential drop across the latter was determined from the potential drop across a 10-ohm standard resistor in series with two 10,000-ohm standard resistors, all of which were in parallel with the calorimeter heater. All the standard resistors were calibrated at intervals of about 1 year by the Resistance Measurements Section of this Bureau.

The potential drops were measured with a White double potentiometer, using saturated standard cells maintained at a constant temperature of 30° C [5, 6]. These cells were made by the Electrochemistry Section of this Bureau and calibrated by them at intervals of about 1 year.

The potentiometer was calibrated by the Electrical Division of this Bureau in 1936, 1942, and 1943. From experiments with electrical energy performed at various times during 1939, 1940, and 1941, a seasonal variation of the apparent energy equivalent of the calorimetric system was found. The magnitude of this variation was equivalent to a maximum variation of 9 in 100,000 in the resistance coils of the potentiometer, if it is assumed that the other parts of the measuring system did not change. The results of the experiments with electrical energy were corrected on the basis of this assumption and the results of the calibration of the potentiometer.

Although the assumption that the parts of the system other than the potentiometer did not change may not be strictly correct, it is consistent with the results of the calibrations of the potentiometer. Also, there are reasons for believing that the high-resistance coils of the potentiometer are affected by varying humidity to a greater ex-

tent than are the other parts of the system [9, 18]. The above method of correcting the results of the experiments with electrical energy is believed to be justified in view of these facts, and in view of the small magnitude of the observed variation in energy equivalent. Recently, the procedure was adopted of checking the potentiometer ratio at the time of each experiment with electrical energy, using two known standard resistors and an auxiliary battery [7].

The entire electrical measuring system was shielded, with copper sheets under the instruments, calorimeter, etc., and with a ground connection to one of the battery leads outside of the measuring circuit, such that the potential difference between the leads to the potentiometer and the ground was as small as possible.

4. TIMING DEVICE

The timing device for determining the time of input of the electrical power was the same as that used in the previous investigations in this laboratory [8]. The current was kept flowing through an external coil of the same resistance as the calorimeter heater. At the appropriate instant, the current was switched into the calorimeter heater and then, at the end of the given time, back to the external "spill" coil. A correction was appropriately applied to the power measurements because of the slightly different resistance of the timing switch circuit during the first two seconds and the last two seconds of the heating from its resistance during the main part of the heating period (see section VI–1). Although negligible (3 parts per million), this correction was made for the sake of completeness.

5. THERMOMETRIC SYSTEM

In the experiments with calorimeter systems A and B, platinum resistance thermometer No. 285,380 was used [4], whereas in the experiments with calorimeter system C a new platinum resistance thermometer No. 373,730 was used. The constants provided for this thermometer by the Thermometry Section of this Bureau yield the following relation for the range 0° to 100° C:

$$R=25.5170+0.101615t-0.00001492t^2 \text{ int. ohms}$$

and

$$dR/dt=0.101615-0.00002984t \text{ int. ohm/degree.}$$

The foregoing equations are used only to determine the temperature to which the observed thermodynamic quantity is to be assigned. A knowledge of the actual relation between resistance and temperature for a given thermometer is not needed for the comparison of electrical energy and chemical energy when the experiments are performed over the same interval of resistance at the same mean temperature.

The resistance bridge used was the same as that previously described [5].

VI. CALORIMETRIC PROCEDURE

1. EXPERIMENTS WITH ELECTRICAL ENERGY

The procedure followed in performing an experiment with electrical energy was as follows: The fuse wire, 0.20 g of soft glass, and 1.00 ml of water were placed in the bomb body and the bomb was closed. The bomb was flushed with purified oxygen to remove the air, the exit valve was closed, and the bomb was filled with oxygen to a pressure of 30 atm at 25° C. The standard mass of water (2,873.26 ± 0.02 g) was weighed in the calorimeter can, which was then placed in position in the calorimeter. The heating coil was placed in position on the bomb body, which was then carefully lowered into the calorimeter can. The latter was then covered with its lid.

The temperature of the jacket was maintained at 28.02° C, constant within ±0.002° C. The experiments were begun with the temperature of the calorimeter near 25.00° C, and the final temperature was made to be slightly below that of the jacket. In the fore period of 20 minutes, readings of the calorimeter temperature were taken every 2 minutes. During the second preceding the end of the 20th minute, the switches on the automatic switching device were set so that the current would be changed from the external stabilizing or "spill" coil to the calorimeter heater when the time signal at 20:00 minutes clicked. At 20:02 the timing device switches were changed from the "temporary" to the "permanent" setting, with no interruption to the flow of current. During the heating period of 5 minutes, readings were taken every minute of the resistance of the platinum thermometer in the calorimeter, the "voltage," and the "current." At 24:58, 2 seconds before the end of the 5-minute heating period, the switches of the timing device were changed from their "permanent" to their "temporary" setting, and at 25:00 the current was automatically changed from the calorimeter heater to the external stabilizing coil.[5] Readings of the resistance of the platinum thermometer were then taken every minute until 36:00 minutes, when the calorimeter again reached a steady state, denoting the end of the "reaction" period. During the "after" period from 36:00 to 56:00 minutes, readings of the resistance of the platinum thermometer were taken every two minutes. After the end of the "after" period, the platinum thermometer was transferred from the calorimeter can to the jacket, and its resistance at the temperature of the jacket was measured.

The calculation of ΔR_c, the corrected increase in temperature of the calorimeter system, expressed as the increase in resistance in ohms of the given platinum resistance thermometer at a mean temperature of 26.50° C, as measured with the given resistance bridge, has been previously described [4]. The amount of electrical energy divided by the value of ΔR_c for the same experiment yields a value of E_s, the electrical energy equivalent of the calorimeter for the standard conditions.

[5] The "temporary" settings are those in which the current flows through the automatic switch, and the "permanent" settings are those in which the current flows through switches which bypass the automatic switch.

2. DETERMINATION OF THE IGNITION ENERGY

The energy added to the calorimeter by the heating and burning of the fuse wire was determined as previously described [4]. The standard process of ignition produced an increase of 0.000411 ohm in the "temperature" of the standard calorimeter system. The fuse was a 5-cm length of "Parr" wire, No. 36 AWG, the "standard" weight of which was 0.00760 g. An alternating current from a 24-volt supply was used for the ignition.

3. COMBUSTION EXPERIMENTS

The procedure followed in performing a calorimetric combustion experiment is described in detail on pages 302 and 303 of reference [4].

4. CORRECTION FOR THE FORMATION OF NITRIC ACID

The value of Δr_n, which is the rise in temperature of the calorimeter system produced by the heat evolved in the formation of a small amount of nitric acid, according to the reaction

$$\frac{1}{2}N_2(g)+\frac{1}{2}H_2O(liq)+\frac{5}{4}O_2(g)=HNO_3(aq)$$

was calculated from the amount of nitric acid formed, using the value 57.8 int. kj/mole for the heat evolved in the formation of dilute aqueous nitric acid in the bomb process. The procedure previously described [4] was followed.

VII. RESULTS OF THE PRESENT INVESTIGATION

1. EXPERIMENTS WITH ELECTRICAL ENERGY

During the course of this extended investigation, three changes were made in the calorimeter system, and there were actually four slightly different calorimeter systems, A, B_1, B_2, and C, with B_1 and B_2 being essentially identical in energy equivalent. The changes consisted in replacing the bronze sleeve (having 10 setscrews, holding the head against the body of the bomb) with a stainless-steel sleeve (having 16 setscrews), the loosely fitting calorimeter heater with one tightly fitting on the bomb body, and platinum resistance thermometer No. 285,380 with No. 373,730, as follows:

System	Sleeve	Heater	Thermometer
A	Bronze	Loosely fitting	No. 285,380
B_1	Stainless steel	do	Do.
B_2	do	Tightly fitting	Do.
C	do	do	No. 373,730

The results of the experiments with electrical energy on systems A, B_1, B_2, and C are given in table 1. The symbols given in the table are defined in the previous reports [4, 8, 10].

TABLE 1.—*Experiments with electrical energy on calorimeter systems*

A. SYSTEM *A* (WITH LOOSELY FITTING HEATER)

Series	Number of experiments	k	K	U	ΔR_e	Electrical energy	E_e	
							Mean	Standard deviation of the mean
		min^{-1}	*Ohm*	*Ohm*	*Ohm*	*Int. j*	*Int. j/ohm*	*nt. j/ohm*
I	17	0.001922 to .001958	0.001690 to .001959	0.000067 to .000314	0.283939 to .294874	[a] 39084.51 to 40587.47	137634.2	±5.0
II	10	.001939 to .001956	.001664 to .002043	.000117 to .000150	.276048 to .292009	[a] 37997.18 to 40196.33	137625.8	±2.4
III	6	.001938 to .001959	.001848 to .001928	.000035 to .000067	.291303 to .293913	[a] 40093.38 to 40449.08	137620.9	±2.6
Weighted mean							[b] 137624.7	±1.7

B_1. SYSTEM B_1 (WITH LOOSELY FITTING HEATER)

I	8	0.001927 to .001955	0.001729 to .001923	0.000131 to .000154	0.285673 to .294785	[a] 39443.91 to 40703.17	[b] 138044.7	±3.2

B_2. SYSTEM B_2 (WITH TIGHTLY FITTING HEATER)

[c] I	4	0.001932 to .001945	0.006607 to .006690	0.000323 to .000371	0.287110 to .289724	[d] 39606.34 to 39970.73	137998.7	±4.2
[c] II	4	.001940 to .001946	.002012 to .002206	.000549 to .000579	.289845 to .297640	[d] 39981.78 to 41058.92	137994.1	±4.2
[c] III	4	.001943 to .001949	.006471 to .006577	.001046 to .001168	.289570 to .290903	[d] 39938.17 to 40127.50	137987.1	±4.7
[c] IV	6	.001960 to .001987	.001385 to .002060	.000330 to .000581	.293368 to .304355	[d] 40478.37 to 41978.61	137987.8	±8.8
Weighted mean							137993.3	±2.4

C. SYSTEM *C* (WITH TIGHTLY FITTING HEATER)

I	7	0.001950 to .001959	0.001928 to .002942	0.000280 to .000364	0.259366 to .295728	[a] 35721.60 to 40736.74	137717.4	±0.8

[a] The time of input of electrical power was 300.00 seconds, with a current of 0.97 ampere.
[b] This value is used only for obtaining the ratio of the energy equivalents of systems *A* and B_1.
[c] The rate of stirring of the calorimeter was 285 rpm in series I, 400 rpm in series II and III, and 350 rpm in series IV.
[d] In series I and III, the time of input of electrical power was 1200.00 seconds, with a current of 0.48 amperes; in series II and IV, the time was 300.00 seconds, with a current of 0.97 ampere.

The data given in table 1A and $1B_1$ yield a precise value for the ratio of the energy equivalents of calorimeter systems A and B_1. However, it was subsequently found, by using lower power and longer time (20 minutes) of heating (see below), that the values of the energy equivalent determined for systems A and B_1 (with the loosely fitting heater) with high power and short time (5 minutes) of heating were, in an absolute sense, too large by several parts in 10,000. It appears that the combination of a high rate of input of electrical energy and a loosely fitting heater of low heat capacity produces conditions in the electrical-energy experiments which are calorimetrically appreciably different from those which exist in the calorimetric combustion experiments, in which the heat is evolved entirely within the bomb. Improvement in this respect can be obtained by using a higher rate of stirring (too high a rate is undesirable because the stirring energy would become too important), by using a lower rate of input of electrical energy (too low a rate is undesirable because it makes the time-temperature relations too different in the electrical-energy experiments and the calorimetric combustion experiments), and by using a heater which fits tightly on the bomb body (which would permit a large part of the electrical energy to be taken up first by the bomb body, simulating a little more closely the conditions in the calorimetric combustion experiments). Accordingly, system B_1 was changed to system B_2 by replacing the loosely fitting heater with one fitting tightly on the bomb body. The systems B_1 and B_2 were identical in every way except for a smaller mass (about 14.5 g less) of copper used in making the tightly fitting heater. The equivalent of 14.5 g of copper was added to system B_2, making the energy equivalent of system B_2 exactly equal to that of system B_1.

The data in table $1B_2$, giving the results of four different series of experiments, provide an accurate value for the energy equivalent of system B_2, and thus also of system B_1. The value, and standard deviation of the mean, for the energy equivalent of system B_2 ($=B_1$) is

$$E_s\ (B_2) = 137{,}993.3 \pm 2.4 \text{ int. j/ohm.}$$

In series I and III (in table $1B_2$) the time of heating was 20 minutes, with a current of approximately 0.48 ampere; whereas in series II and IV the time of heating was 5 minutes, with a current of approximately 0.97 ampere. With the absolute value of the energy equivalent of system B_2 established from the experiments reported in table $1B_2$, and with that for system B_1 taken (after appropriate adjustment) as equal to that of system B_2, the energy equivalent of system A was calculated from the value for system B_2 and the ratio for systems A and B_1 as given by the values in table 1A and $1B_1$. The value, and standard deviation of the mean, for the energy equivalent of system A becomes

$$E_s\ (A) = 137{,}573.5 \pm 4.3 \text{ int. j/ohm.}$$

The data given in table 1C yield an accurate value for the energy equivalent of calorimeter system C (in terms of its new thermometer)

System C, as previously reported, differed from system B_2 only in the thermometer used. The value, and standard deviation of the mean, for the energy equivalent of system C is

$$E_s\ (C)=137{,}717.4\pm0.8 \text{ int. j/ohm.}$$

A number of experiments with benzoic acid [16] made on the three calorimeter systems yielded values for the ratios of their energy equivalent which were equal to the ratios below within their respective limits of uncertainty. Also, the value for the heat of combustion of benzoic acid under the standard conditions of the bomb process is in excellent agreement with the most recent value reported by Jessup [17]. The data of six experiments on system A, with a heating period of 20 minutes, yielded a value, and standard deviation of the mean, for the energy equivalent of system A of $137{,}572.9\pm0.9$ int. j/ohm, which energy equivalent is essentially identical with the value given above for $E_s\ (A)$.

As it was found desirable to present the data of the combustion experiments (see next section) in terms of the final calorimeter system, C, the following relations were used to make the conversion:

$$E_s\ (A)=0.998955E_s\ (C)$$

$$E_s\ (B)=1.002003E_s\ (C).$$

The over-all uncertainty assigned to the value of the energy equivalent of calorimeter system C, in terms of which all the data are reported, was taken as twice the standard deviation of the mean of the least precise series of measurements (those of system A), ±0.006 percent, together with an estimated uncertainty of ±0.010 percent allowed for errors in calibration of the electrical measuring instruments, yielding, as the square root of the sum of the squares, ±0.012 percent as the over-all uncertainty for the experiments with electrical energy. The energy equivalent of system C, with its over-all uncertainty, was taken, therefore, as

$$E_s\ (C)=137{,}717.4\pm16.5 \text{ int. j/ohm.}$$

2. COMBUSTION EXPERIMENTS

The results of the combustion experiments on *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-dodecane, and *n*-hexadecane are given in table 2. The symbols at the heads of the columns are as previously defined [4, 8, 10]. For simplicity in presenting and handling the data, all the values of the constant B are given in terms of the energy equivalent of system C, using the conversion factors given in the preceding section.

TABLE 2.—*Results of calorimetric combustion experiments on n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-dodecane, and n-hexadecane, in the liquid state*

Substance	Series	No. of experiments *				Mass of carbon dioxide formed	k	K	U	ΔR_s	r_t	r_n	B	
		A	*B*	*C*	Total								Mean	S. d. of the mean
						g	min^{-1}	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*		
n-Pentane	I		5			1.92349 to 2.33112	0.001929 to .001945	0.001462 to .002844	0.000082 to .000122	0.222264 to .269272	0.000415 to .000424	0.000069 to .000085	0.1155367	±0.0000040
	II			5		2.69047 to 2.81812	.001942 to .001956	.000134 to .000769	.000304 to .000370	.311213 to .325767	.000408 to .000422	.000047 to .000050	.1155193	±.0000225
	III			4		2.14596 to 2.57252	.001933 to .001963	.000985 to .002374	.000302 to .000354	.248416 to .297540	.000404 to .000414	.000018 to .000020	.1155269	±.0000165
	All				14								.1155277	±.0000089
n-Hexane	I	4				2.23988 to 2.61928	.001927 to .001935	.000785 to .001974	.000080 to .000138	.256553 to .299854	.000398 to .000428	.000027 to .000028	.1142150	±.0000113
	II	6				2.46001 to 2.72779	.001929 to .001943	.000741 to .001255	.000098 to .000152	.281662 to .312217	.000415 to .000421	.000027 to .000028	.1142096	±.0000070
	III			2		2.30521 to 2.35264	.001951 to .001949	.001963 to .001810	.000344 to .000339	.263831 to .269246	.000417 to .000422	.000042 to .000043	.1142580	±.0000015
	All				12								.1142194	±.0000071
n-Heptane	I	6				2.19539 to 2.67843	.001944 to .001954	.000634 to .001473	.000101 to .000206	.249413 to .304151	.000363 to .000415	.000028 to .000090	.1132717	±.0000063
	II		7			2.20202 to 2.71804	.001948 to .001964	.000709 to .002310	.000278 to .000422	.249606 to .307941	.000404 to .000434	.000039 to .000093	.1133118	±.0000060
	III			7		2.46740 to 2.74361	.001943 to .001956	.000660 to .001539	.000331 to .000365	.279935 to .311208	.000412 to .000431	.000044 to .000048	.1132818	±.0000067
	All				20								.1132893	±.0000052
n-Octane	I		4			2.39215 to 2.70168	.001937 to .001944	.000418 to .001718	.000070 to .000214	.269297 to .323369	.000406 to .000420	.000081 to .000098	.1125849	±.0000080
	II			6		2.45376 to 2.60154	.001952 to .001957	.001340 to .002160	.000304 to .000365	.255416 to .293292	.000400 to .000421	.000020 to .000047	.1125785	±.0000092
	All				10								.1125810	±.0000062
n-Nonane	I			4	4	2.39401 to 2.51462	.001948 to .001954	.001490 to .001855	.000293 to .000325	.268631 to .282141	.000405 to .000416	.000038 to .000042	.1126402	±.0000083

	All				10	2.60154	.001957	.002160	.000365	.263292	.000421	.000047	.1125810	±.0000062
n-Nonane	I			4	4	2.39401 to 2.51462	.001948 to .001954	.001490 to .001855	.000293 to .000325	.268631 to .282141	.000405 to .000416	.000038 to .000042	.1120402	±.0000083
n-Decane	I			5	5	2.40661 to 2.73230	.001941 to .001981	.000598 to .001857	.000264 to .000336	.268970 to .305394	.000369 to .000422	.000037 to .000045	.1116005	±.0000089
n-Dodecane	I		5			2.55905 to 2.72789	.001947 to .001962	.000744 to .001267	.000131 to .000274	.283846 to .302609	.000411 to .000423	.000080 to .000085	.1109474	±.0000088
	II			1		2.60799	.001957	.001279	.000338	.289788	.000422	.000040	.1109520	
	All				6								.1109482	±.0000073
n-Hexadecane	I		5			2.47957 to 2.87824	.001935 to .001959	.000326 to .001587	.000085 to .000142	.272915 to .316764	.000401 to .000417	.000076 to .000084	.1101145	±.0000055
	II			2		2.76644 to 2.66958	.001954 to .001954	.000853 to .001145	.000349 to .000318	.305062 to .294408	.000424 to .000413	.000043 to .000037	.1101235	±.0000043
	All				7								.1101171	±.0000042

* The numbers in the columns labeled *A*, *B*, and *C* indicate the number of experiments performed with calorimeter systems *A*, *B*, and *C* (see section V–1, section VII–1, and table 1.

3. VALUES OF THE HEATS OF COMBUSTION

In table 3 are presented the resulting values of the heats of combustion of the eight normal paraffin hydrocarbons from the present investigation. There are given the value of the constant B for 28° C, in ohms per gram of carbon dioxide, as defined by eq 4 of reference [4]; $-\Delta U_B$, the heat evolved in the bomb process at 28° C, in international kilojoules per mole of hydrocarbon; $-\Delta U_R°$, the decrement in internal energy for the ideal reaction of combustion at 28° C, with all the reactants and products in their standard states; $-\Delta Hc°$, the decrement in heat content (or heat evolved in the combustion at constant pressure) for the reaction of combustion of the liquid hydrocarbon at 28° C, with all the reactants and products in their standard states; and, finally, the same quantity, $-\Delta Hc°$, for the reaction of combustion at 25° C. The foregoing values of $-\Delta U_R°$ and $-\Delta Hc°$ apply to the reaction

$$C_nH_{2n+2}(\text{liq})+\frac{3n+1}{2}O_2(\text{gas})=nCO_2(\text{gas})+(n+1)H_2O(\text{liq}).$$

TABLE 3.—*Values of the heats of combustion*

TABLE 3.—*Values of the heats of combustion*

Substance	*B* at 28.00° C	$-\Delta U_B$ at 28° C	$-\Delta U_B°$ at 28° C	$-\Delta H_c°$ (liq) at 25° C	$-\Delta H_c°$ (liq) at 25° C
	Ohms/g CO_2	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*	*kcal/mole*
n-Pentane	0.1155277 ±0.0000178	3501.03 ±0.77	3500.34 ±0.77	3507.85 ±0.77	838.71 ±0.18
n-Hexane	.1142194 ±.0000142	4153.66 ±.83	4152.75 ±.83	4161.51 ±.83	994.99 ±.20
n-Heptane	.1132693 ±.0000104	4806.48 ±.87	4805.40 ±.87	4815.41 ±.87	1151.33 ±.21
n-Octane	.1125810 ±.0000124	5458.78 ±1.05	5457.48 ±1.05	5468.75 ±1.05	1307.64 ±.25
n-Nonane	.1120402 ±.0000106	6111.62 ±1.12	6110.19 ±1.12	6122.71 ±1.12	1463.80 ±.27
n-Decane	.1116005 ±.0000178	6764.04 ±1.52	6762.40 ±1.52	6776.17 ±1.52	1620.13 ±.36
n-Dodecane	.1109452 ±.0000146	8069.41 ±1.65	8067.40 ±1.65	8083.67 ±1.65	1932.73 ±.39
n-Hexadecane	.1101171 ±.0000084	10678.62 ±2.80	10675.86 ±2.80	10697.14 ±2.80	2557.58 ±.68

As stated in section III, the over-all uncertainty assigned to each final value of the heat of combustion of a given compound was taken as the square root of the sum of the squares of the following: (*a*) Twice the standard deviation of the mean of the series of combustion experiments, (*b*) an uncertainty of 0.010 percent in the determination of the absolute value of the amount of reaction, (*c*) twice the standard deviation of the mean (or weighted mean) of the series of experiments with electrical energy, and (*d*) an uncertainty of 0.010 percent in the determination of the absolute value of the amount of electrical energy.

VIII. DISCUSSION

The values of the heats of combustion reported here will be discussed in another report in connection with their relation to the existing data, the selection of "best" values for the heats of combustion, and the evaluation of the increment in energy per CH_2 group, for the normal paraffin hydrocarbons.

IX. REFERENCES

[1] E. F. Mueller and F. D. Rossini, Am. J. Phys. **12,** 1 (1944).
[2] G. P. Baxter, M. Guichard, O. Hönigschmid, and R. Whytlaw-Gray, J. Am. Chem. Soc. **63,** 845 (1941).
[3] F. D. Rossini and W. E. Deming, J. Wash. Acad. Sci. **29,** 416 (1939).
[4] E. J. Prosen and F. D. Rossini, J. Research NBS **27,** 289 (1941) RP1420.
[5] F. D. Rossini and J. W. Knowlton, J. Research NBS **19,** 249 (1937) RP1024.
[6] E. F. Mueller and H. F. Stimson, J. Research NBS **13,** 699 (1934) RP739.
[7] N. S. Osborne, H. F. Stimson, and D. C. Ginnings, J. Research NSB **23,** 197 (1939) RP1228.
[8] F. D. Rossini, BS J. Research **6,** 1 (1931)RP259.
[9] F. B. Silsbee and F. J. Gross, J. Research NBS **27,** 269 (1941) RP1419.
[10] J. R. Eckman and F. D. Rossini, BS J. Research **3,** 597 (1929) RP111.
[11] M. Shepherd and H. W. Bailey, J. Research NBS **26,** 347 (1941) RP1381.
[12] A. R. Glasgow, Jr., and F. D. Rossini, National Bureau of Standards. Unpublished.
[13] B. J. Mair, BS J. Research **9,** 457 (1932) RP482.
[14] B. J. Mair and A. J. Streiff, J. Research NBS **24,** 395 (1940) RP1289.
[15] E. J. Prosen and F. D. Rossini, J. Research NBS **27,** 519 (1941) RP1439.
[16] E. J. Prosen and F. D. Rossini, J. Research NBS (publication pending).
[17] R. S. Jessup, J. Research NBS **29,** 247 (1942) RP1499.
[18] E. B. Rosa and H. D. Babcock, Bul. BS **4,** 121 (1907–8) S73.

WASHINGTON, June 10, 1944.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1608

Part of Journal of Research of the National Bureau of Standards, Volume 33, October 1944

LIQUID-JUNCTION POTENTIALS, AND RELATIVE ACTIVITY COEFFICIENTS OF CHLORIDE IONS, IN CONCENTRATED MIXED CHLORIDES AND NITRATES AT 25° C

By George G. Manov, Nicholas J. DeLollis, and S. F. Acree

ABSTRACT

Measurements are reported of the electromotive forces at 25° C of pairs of calomel half-cells in which portions of the saturated potassium chloride had been replaced at constant ionic strength (4.831) by hydrochloric acid and potassium nitrate. The method of cells with liquid junctions was used.

Data are given for the stability of half-cells prepared with these electrolytes, for the reproducibility of the liquid junction and the calculated value of its potential, and for the activity coefficient of the chloride ion in these mixtures relative to that of saturated potassium chloride solution. The addition of hydrochloric acid raises and the addition of potassium nitrate lowers the mean activity coefficient of chloride ion in potassium chloride solutions. Because the difference between the effective ionic mobilities for the cations and the anions in these solutions is smaller than in saturated potassium chloride alone, such cells are useful as reference electrodes in the reduction of the error caused by the neglect of the liquid-junction potential in the determination of pH by electrometric methods.

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I. INTRODUCTION

Calomel reference half-cells in combination with hydrogen, glass, or other electrodes are very convenient and are widely used for the determination of pH values by electrometric methods. The ideal reference half-cell is one with a stable, reversible electrode (AgCl, Hg_2Cl_2), without hysteresis, with a low emf-temperature coefficient, and whose electrolyte is very concentrated and isoelectric, that is, of such composition that equal numbers of positive and negative charges diffuse into its junction with another liquid whose pH is to be determined. The saturated (4.831 *m*) potassium chloride-calomel half-cell fulfills most of those requirements, but the chloride ion has a mobility slightly greater than that of the potassium ion and the liquid is approximately 1.1 mv (0.02 pH unit) positive toward its sharp junction with an isoelectric solution. A source of error, there-

fore, arises from the potential at the liquid junction between the two solutions surrounding the reference and hydrogen electrodes, respectively. This potential is a variable because of the differences in the rates of diffusion of the ions which compose the various solutions forming the liquid junctions in pH measurements. This uncertainty of the liquid-junction potential may cause large errors in extreme cases [1][1] when the buffer solution used to calibrate the pH meter is replaced by a highly acid or alkaline solution whose ionic constituents and pH value are not known.[2] For work within 0.01 pH, therefore, it is desirable to know how to reduce the liquid-junction potential to less than 1 mv toward average and specific types of solutions. This can be done by changing the composition of the solution in the reference-electrode compartment. The error caused by the liquid-junction potential can be further diminished by the selection of a standardizing buffer, which approximates the pH and the composition of the unknown solution.

The existence of these potentials has long been known, and the problem of their reduction has been studied for more than 50 years.[3] The equations developed by Planck [4] and by Henderson [5] constitute the most important theoretical advances in the field, and are regarded as being the two most practical methods for the calculation of the potential at the liquid junction.

In 1931 Murray and Acree [6] proposed the use of potassium chloride and nitrate in a molal ratio of 3:1 alone and the use of this mixture with dilute hydrochloric acid for the electrolyte in the calomel half-cell. For such a mixture, the effective anion and cation mobilities are very nearly equal. Consequently the contribution to the contact potential by this electrolyte should be lower than for saturated potassium chloride alone.

The present investigation was made to obtain data on the stabilities and the differences in the potentials at 25° C of calomel half-cells in which potassium nitrate and hydrochloric acid replaced a part of the saturated potassium chloride in the electrolyte at constant ionic strength, 4.831. Three mixtures of these electrolytes in calomel half-cells made stable reference electrodes and were better than potassium chloride alone in reducing liquid-junction potentials. A further purpose of this investigation was to determine the relative activity coefficients of chloride ion in these mixed electrolytes, and the variation of the liquid-junction potentials of these solutions for fixed and flowing junctions of the "pig-tail" type [3].

II. EXPERIMENTAL METHODS

1. SOLUTIONS, EQUIPMENT, AND ELECTRODES

The solutions were prepared from weighed quantities of conductivity water and reagent-grade chemicals conforming to the specifications of the American Chemical Society. The densities of the solutions were determined at 25° C by means of a Westphal balance and were used for converting the molal to the molar scales of concentration. The data are given in table 1.

[1] Figures in brackets indicate the literature references at the end of this paper.
[2] Although pH values can be measured by means of cells without liquid junctions [2], a more detailed knowledge of the composition of the solution is required than is usually available.
[3] A review of the literature up to 1932 has been given by Kline, Meacham, and Acree [3].

TABLE 1.—*Composition and density of solutions used as electrolytes in cells with liquid junctions*

Solution	HCl	KCl	KNO_3	Total	Density at 25° C
	Moles per thousand grams of water				
					g/ml
A		4.831		4.831	1.1783
B		3.623	1.208	4.831	1.1924
C	0.050	3.573	1.208	4.831	1.1910
D	.050	4.781		4.831	1.1780
	Moles per liter of solution				
A		4.185		4.185	
B		3.103	1.035	4.138	
C	0.043	3.061	1.035	4.139	
D	.043	4.147		4.190	

The electromotive forces were measured by means of a precision type of potentiometer and a standard cell, both calibrated at this Bureau. All measurements were made in an air bath at 25° ±0.1° C.

The calomel half-cells (fig. 1) were Pyrex cylinders, *A*, approximately 2 cm in diameter and 7 cm tall, with a glass partition, *B*, extending 2.5 cm upward from the bottom of the cylinder and dividing the latter into two separate compartments, or half-cells. Tungsten leads, *C*, were introduced through the bottom of each half-cell. Two such units were connected by means of a tube approximately 1 cm in diameter. A stopcock, *D*, admitted the electrolyte to the cell. The hollow ground-glass stopper, *E*, was weighted with mercury.

The liquid-junction chamber, *A* in figure 2, was of the same general type used previously [3] but was separate from the half-cells and could be removed without disturbing them. The functions of stopcocks *H*, *I*, and *J* in figures 2 and 3 are explained later.

The mercury for use in the half-cells was washed repeatedly with 10-percent nitric acid and then twice distilled. The calomel electrodes were prepared in accordance with the recommendations of Wingfield and Acree [7]. The emf of new and aged cells of the same type differed at first by approximately 0.2 mv, but after approximately 12 hours this difference was reduced to 0.03 mv or less.[4]

No further change greater than ±0.02 mv was observed over a test period of 26 days. The aging period did not vary significantly for cells prepared with the different electrolytes listed in table 1.

The assembled apparatus is shown in figure 3. *A* and *B* are the calomel half-cells, and bulbs *C* and *D* are the corresponding reservoirs. Each was filled with one of the particular solutions under investigation; bulb *E* contained the less dense solution (generally the same as in *D*) to which had been added a small amount of an indicator (solid methyl orange) or a dye (alpha azurine *G*) to render the liquid junction more easily visible. Because the denser solution was always introduced through the "pig-tail", two such liquid junction chambers, *L* and *L'* were provided to facilitate the emf measurements on different pairs of solutions in any sequence.

[4] In a detailed study of the preparation of calomel electrodes, Clarke, Myers, and Acree [8] found that an aging period of 2 days was necessary to attain an agreement of ±0.03 mv between new and aged electrodes. The shorter period of time observed in the present work may be attributed to technical advances in the manufacture of intimate mixtures of mercurous chloride and mercury. A variation of ±0.03 mv in emf corresponds to ±0.0005 in pH.

The solutions were admitted to the calomel half-cells and then to the liquid-junction chambers through stopcocks *F*, *G*, and *H*, and the entrapped air removed through stopcock *I*. Stopcock *I* was then closed, and stopcock *J* opened. The relative quantities of the heavier and of the lighter solutions entering the liquid-junction chamber were governed by the positions of stopcocks *F* and *G*, respectively, and the position of the boundary in the liquid-junction chamber could therefore be varied at will. Sharp junctions were obtained even when the rates of flow were varied widely. The combined solutions were discarded through the tip *K* into a graduated cylinder, which was used to measure the rates of flow.

2. ELECTROMOTIVE FORCES OF CELLS WITH LIQUID JUNCTIONS

In table 2 are given the data obtained for the cell

$$-\mathrm{Hg}\,|\,\mathrm{Hg_2Cl_2}\,|\,\mathrm{KCl}(4.831\ \mathrm{m})\|\mathrm{KCl}(3.623\ \mathrm{m})+\mathrm{KNO_3}(1.208\ \mathrm{m})\,|\,\mathrm{Hg_2Cl_2}|\mathrm{Hg}+ \quad (1)$$

When current is withdrawn from this cell, the reaction[5] is

$$\mathrm{Cl^-(in\ KCl)}\|\mathrm{Cl^-(in\ KCl+KNO_3)};E_t=+8.74\ \mathrm{mv}, \quad (2)$$

where the symbol ‖ indicates the presence of a liquid-junction potential, and E_t is the measured emf of the cell. The over-all electromotive force of any given cell combination was found to be independent to within ±0.01 mv of the total and the relative rates of flow of the two electrolytes, the position of the liquid junction in the pig-tail chamber, the order in which the electrolytes were admitted, and of the indicator or dye added. The emf of duplicate pairs of cells checked to within ±0.03 mv.

TABLE 2.—*Observed electromotive force at 25° C of a typical cell*

[Electrolyte *A*: 4.831 moles of KCl per 1,000 g of water. Electrolyte *B*: 3.623 moles of KCl and 1.208 moles of KNO_3 per 1,000 g of water]

Rate of flow of electrolyte			Electromotive force of cell	Junction
A	*B*	*A*+*B*		
ml/min	*ml/min*	*ml/min*	*mv* [a]	
¼	0	¼	8.72	Rising.
½	¼	½	8.73	Steady.
¼	½	¾	8.74	Falling rapidly.
½	35½	36	8.73	Rising rapidly.
35½	½	36	8.73	Fixed.
0	0	0	8.73	Rising rapidly.
0	25	25	8.74	Falling rapidly.
25	0	25	8.74	Steady.
25	25	50	8.74	Fixed.
0	0	0		
Average			8.74	

[a] Measurements made with a small amount of dye added to solution *B* showed the same degree of constancy.

[5] In tables 2, 3, and 5 the sign of the total emf or of the liquid-junction potential is that of the electrode in the second solution, designated as *A*, *B*, etc., in table 1. The liquid-junction potential of the cell described in eq 2, for example, is −0.22 mv.

In table 3 a summary is given of the measured emf of each of the six possible cells that can be formed by the combination in pairs of the half-cells containing electrolytes *A* to *D*, inclusive. The statements made regarding the constancy of the emf, etc. of the cell described in eq 1 apply equally well to each of the additional measurements listed in this table.

TABLE 3.—*Summary of electromotive force measurements at 25° C*

Solutions	Electrolytes	Electromotive force
		mv
A, B	KCl versus KCl+KNO_3	8.74 ±0.02
A, C	KCl versus KCl+KNO_3+HCl	8.16 ±0.02
A, D	KCl versus KCl+HCl	−0.61 ±0.03
B, C	KCl+KNO_3 versus KCl+KNO_3+HCl	−.61 ±0.02
B, D	KCl+KNO_3 versus KCl+HCl	−9.29 ±0.02
C, D	KCl+KNO_3+HCl versus KCl+HCl	−8.73 ±0.02

III. CALCULATION OF THE LIQUID-JUNCTION POTENTIAL

The potential E_j at the junction of two different solutions, I and II, is given by the equation

$$E_j = -(RT/F)\sum \int_{\mathrm{I}}^{\mathrm{II}} (t_k/z_k)(d \ln a_k) \qquad (3)$$

where t_k, z_k, and A_k are, respectively, the transference number, valence, and activity of a particular ion k, and R, T, and F are recognized constants. The integrations are made separately for each of the ions of which the boundary is composed. With the aid of certain simplifying assumptions, Planck [4] and Henderson [5] have integrated this equation for the "constrained diffusion" and the "continuous mixture" types of boundaries. The former type does not apply to the experimental work reported here and has not been considered further. For the case in which the ions are all univalent, the integration of eq 3 by Henderson reduces to

$$E_j = \frac{RT}{F} \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1 + V_1) - (U_2 + V_2)} \ln \frac{U_1 + V_1}{U_2 + V_2}, \qquad (4)$$

where

$$U_1 = C_k^{+\prime} U_k^{+\prime},\ V_1 = C_k^{-\prime} U_k^{-\prime},\ U_2 = C_k^{+\prime\prime} U_k^{+\prime\prime},\ \text{and}\ V_2 = C_k^{-\prime\prime} U_k^{-\prime\prime}.$$

The single and double primes in the superscripts refer to the ions in the two solutions which form the boundary. C_k and U_k are, respectively, the concentration in moles per liter and the mobility of the ion k. The positive and negative signs refer to the charges on the ions.

The Henderson integration (eq 4) involves three assumptions: the mobility of an ion (a) does not change with concentration and (b) is not affected by the presence of other ions, and (c) the electrolytes are completely dissociated and the activity coefficient of each ion is unity in mixtures of ions at all concentrations. Each of these assumptions is questionable.

Measurements of the changes of ionic mobilities and of transference numbers with concentration have been made for simple solutions such as potassium chloride, but the corresponding data for mixtures of electrolytes are meager. None are available for the mixtures studied here. Longsworth [9] measured at 25° C the mobilities of the ions in mixtures of hydrochloric acid and potassium chloride in which the total molality was 0.1. The equivalent conductance of the chloride ion, for example, was found to vary linearly between the limits 65.98 and 65.79, respectively, with the mole fraction in mixtures of 0.1-*m* hydrochloric acid and 0.1-*m* potassium chloride. It is wholly speculative to assume that this linear relationship is valid for concentrations as high as 4.831 *m*, and until the data become available there is no choice other than to use the first two assumptions employed by Henderson. Additional conductance and transference measurements for mixtures of ions are needed.

The assumption regarding the activity coefficient is amenable to correction, but for the solutions studied here the entire effect is negligible. With the customary definition

$$a_k = m_k f_k, \tag{5}$$

where f_k is the activity coefficient of the ion k, eq 3 may be integrated to give

$$E_j = E_{\text{Henderson}} - \frac{RT}{F}\sum \int_{\text{I}}^{\text{II}} \frac{t_k}{z_k}(d \ln f_k) = E_{\text{Henderson}} + E_f. \tag{6}$$

The activity coefficient, f_k, can be expressed by the modified Debye-Hückel equation

$$\log f_k = \frac{-A\mu^{1/2}}{1+Ba_i\mu^{1/2}} + D\mu + E\mu^2. \tag{7}$$

The values of D and E can be obtained empirically or can be estimated from the co-volume effect [10]. In theory, the integral in eq 6 could be evaluated by use of eq 7 and the dependence of t_k upon C, but in practice it is found that the new integrals thus obtained are so complex that the effort is not warranted.

The graphical integration can be performed quite readily in the manner suggested by Harned [11].[6] The details of the procedure for the calculation of the integral in eq 6 for each ion in the junction

$$\text{KCl}(4.831\ m)\|\text{HCl}(0.05\ m)+\text{KCl}(4.781\ m) \tag{8}$$

are as follows. First the transference numbers of H^+, K^+, and Cl^- are computed from the ionic mobilities [7] and the concentrations for mixtures of x parts of hydrochloric acid and potassium chloride (solution D) and $(1-x)$ parts of potassium chloride (solution A). Then values of $\log f$ must be computed for each ion. Hawkins [15] has measured at 25° C the emf of the cell

$$-\text{H}_2|\text{HCl}\ m_1,\ \text{KCl}\ m_2|\text{AgCl}|\text{Ag}^+, \tag{9}$$

[6] The method has been applied to electrometric titrations by Hamer and Acree [12] and to halide cells in general by Hamer [13].

[7] The values of the mobilities at infinite dilution taken from the compilation of MacInnes [14] are for hydrogen, potassium, chloride, and nitrate ions, respectively, 349.82, 73.52, 76.34, and 71.44.

in which m_1+m_2 was kept constant in any one series of experiments over the range 0.1 to 6.0 in ionic strength. The results have been put into algebraic form by Harned [16]:

$$\log f_1=\alpha_1 m_1+\log f_1^*=\log f_{1(0)}-\alpha_1 m_1, \tag{10}$$

and

$$\log f_2=\alpha_2 m_2+\log f_2^*=\log f_{2(0)}-\alpha_2 m_2, \tag{11}$$

where the subscripts 1 and 2 refer to the acid and to the salt in the same mixture; $f_{1(0)}$ and $f_{2(0)}$ are the activity coefficients of pure hydrochloric acid and potassium chloride solutions; f_1^* and f_2^* are the activity coefficients of vanishingly small quantities of hydrochloric acid in solutions of potassium chloride and of potassium chloride in solutions of hydrochloric acid; and α_1 and α_2 are constants. For values of $m_1+m_2=4.831$, and at a temperature of 25° C, $\log f_1^*=0.3485$, $\log f_2^*=-0.2273$, $\alpha_1=0.0710$, and $\alpha_2=-0.032$. Values of $\log f_{HCl}$ and $\log f_{KCl}$ at an ionic strength of 4.831 were then obtained for these mixtures which are predominantly KCl.

Two procedures are commonly used to estimate individual activity coefficients in mixtures of electrolytes. In the first of these, that of MacInnes [17], it was assumed that for pure solutions of potassium chloride, $f_K=f_{KCl}=f_{Cl}$, where f_{KCl} is the mean activity coefficient of this salt, and that these individual activity coefficients are not altered as a result of partial substitution by other ions at constant ionic strength. From the definition of the mean activity coefficient it follows that for these mixtures $f_H=(f_{HCl})^2/f_{Cl}$. This may be designated as procedure 1. The second procedure is that of Guggenheim [18], in which the activity coefficient of an ion is assumed equal to the mean activity coefficient of the electrolyte of which it is a part. For this case, $f_H=f_{HCl}$ and $f_K=f_{KCl}$, but no information is made available concerning the activity coefficient of chloride ion in these mixed chloride solutions. One may assume that $f_{Cl}=f_{KCl}$, as before (procedure 2a). Another assumption would be that $\log f_{Cl}$ varies linearly with the mixing fraction x between the limits of the averages of $\log f_{HCl}+\log f_{KCl}$ for these solutions. This is equivalent to the assumption that (in mixture) $f_{Cl}=[(f_{HCl})(f_{KCl})]^{\frac{1}{2}}$ (procedure 2b). Other postulates that might be made of the relations between the activity coefficients of the ions would lead to other sets of values for f_H, f_K, f_{Cl} and E_f. The values of $\log f_H$, $\log f_K$, and $\log f_{Cl}$, respectively, which are needed for the graphical integration of $(RT/F)(t_k/z_k)(d \ln f_k)$ in eq 6 by procedures 1, 2a, and 2b, are identical with those given in columns 7, 6, and 5; 5, 6, and 6; and 5, 6, and 8 of table 4 and are represented graphically in figure 4. The integrations yield, respectively, −0.004, −0.002, and −0.002 mv for hydrogen ion, −0.043 mv (identical for all three methods) for potassium ion, and −0.045, −0.045, and −0.075 mv for chloride ion.

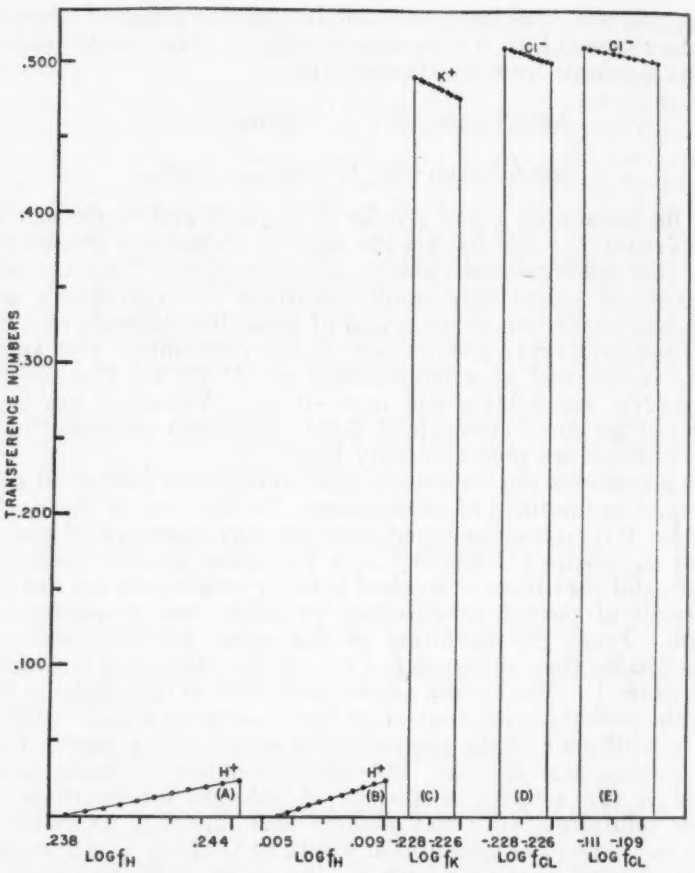

FIGURE 4.—*Evaluation of* $\int t_k \, d \log f_k$ *at 25° C for the ions of mixtures of potassium chloride and hydrochloric acid.*

Areas *A* and *B* correspond to procedures 1 and 2a, and 2b, respectively, for the hydrogen ion; *C*, for the potassium ion by all three procedures; *D* and *E*, for the chloride ion by procedures 1 and 2a, and 2b, respectively.

TABLE 4.—*Values of the quantities required for the computation of* $\int_I^{II} t_k \, (d \log f_k)$ *at 25° C for mixtures of potassium chloride and hydrochloric acid-potassium chloride solutions*

Mixing fraction, x	t_H	t_K	t_{Cl}	$\log f_{HCl}$	$\log f_{KCl}$	$\log f_H$	$\log f_{Cl}$
1	2	3	4	5	6	7	8
0.0	0.0000	0.4906	0.5094	0.0055	−0.2277	0.2385	−0.1111
.1	.0024	.4892	.5084	.0059	.2275	.2392	.1109
.2	.0048	.4877	.5075	.0062	.2274	.2398	.1106
.3	.0072	.4863	.5065	.0066	.2272	.2404	.1104
.4	.0096	.4849	.5055	.0069	.2271	.2409	.1101
.5	.0120	.4834	.5046	.0073	.2269	.2415	.1099
.6	.0143	.4820	.5036	.0076	.2268	.2420	.1096
.7	.0167	.4806	.5027	.0080	.2266	.2426	.1094
.8	.0190	.4793	.5018	.0083	.2265	.2432	.1091
.9	.0214	.4778	.5008	.0087	.2263	.2437	.1088
1.0	.0237	.4764	.5000	.0091	.2262	.2443	.1086

Values at 25° C of the integral in eq 6 for hydrogen, potassium, and chloride ions are totalled according to the equation

$$E_j=-\frac{RT}{F}\sum\int_{\mathrm{I}}^{\mathrm{II}}\frac{t_k}{z_k}(d\ln f_k)$$

$$=-2.303\frac{RT}{F}\left[\int_{\mathrm{I}}^{\mathrm{II}}t_{\mathrm{H}}(d\log f_{\mathrm{H}})+\int_{\mathrm{I}}^{\mathrm{II}}t_{\mathrm{K}}(d\log f_{\mathrm{K}})-\int_{\mathrm{I}}^{\mathrm{II}}t_{\mathrm{Cl}}(d\log f_{\mathrm{Cl}})\right] \quad (12)$$

and yield +0.002, +0.000, and +0.030 mv, respectively, by the three procedures for the value of E_j for the junction depicted in eq 8. There is no a priori reason for the preferential selection of any one of these procedures because of the assumptions common to all. The average correction $E_j=+0.011$ mv is within the experimental reproducibility of the emf of the cells. The above is proof of the statement made earlier in this paper that the inclusion of the terms involving the activity coefficients is a negligible correction to the simple Henderson equation for the solutions studied here. The consistent use of concentrations expressed in moles per kilogram of water instead of moles per liter of solution makes no difference in these conclusions, as values of E_j computed by these two procedures are identical within 0.01 mv. For those cases in which the numerator or the denominator becomes zero and eq 4 is indeterminate, the reduced form [18]

$$E_j=(RT/F)[(U_1-V_1)-(U_2-V_2)]/(U_1+V_1) \quad (13)$$

should be used. The liquid-junction potentials have therefore been calculated by means of eqs 4 and 13 and are given in column 3 of table 5.

TABLE 5.—*Values of the liquid-junction potential (E_j) at 25° C calculated by the Henderson equation, and ratios of the activity coefficients of chloride ion in mixed chlorides*

Solutions in contact	E_{total}	E_j	$\frac{(E_{\text{total}}-E_j)}{59.14}$	$\log\frac{m_{\text{Cl I}}}{m_{\text{Cl II}}}$	$\log\frac{f_{\text{Cl I}}}{f_{\text{Cl II}}}$	$\frac{f_{\text{Cl I}}}{f_{\text{Cl II}}}$
A, B	8.74	−0.22	0.1515	0.1249	0.0266	1.0631
A, C	8.16	−.70	.1498	.1249	.0249	1.0590
A, D	−0.61	−.48	−.0022	.0000	−.0022	0.9950
B, C	−.61	−.49	−.0020	.0000	−.0020	.9953
B, D	−9.29	−.28	−.1523	−.1249	−.0274	.9388
C, D	−8.73	.21	−.1512	−.1249	−.0262	.9414

Calculations of the liquid-junction potentials of solutions *A*, *B*, *C*, and *D* against a hypothetical isoelectric solution of ionic strength 4.831 composed of univalent ions having mobilities equal to the average of those of the potassium and chloride ions yield −1.11, −0.27, +0.19, and +0.02 mv, respectively, for E_j. It is interesting to note that solution *D* is very nearly isoelectric, and that solutions *B*, *C*, and *D* are all better than pure saturated potassium chloride for the reference electrolyte. Because of the assumptions made in the use of the Henderson equation, it is questionable whether the values given for E_j in table 5 can be improved until an opportunity is had to investigate thoroughly the more rigorous procedure suggested by Murray and Acree [6]. The method involves using two buffer so-

lutions of known pH and chloride concentrations and measuri the four possible emf between the hydrogen and the silver-silver-chl ride or calomel electrodes which are immersed in each of the two sol tions forming the liquid junction. A contact-potential eliminator then interposed between the two buffer solutions and emf da again obtained. Both the electrode and liquid-junction potenti can be thus computed.

IV. RELATIVE ACTIVITY COEFFICIENTS OF CHLORID ION IN MIXED ELECTROLYTES

The over-all emf of a cell involving a liquid junction is the sum three separate contributions: the emf generated at the two electrod and that at the liquid junction. For a cell such as depicted in eq the total electromotive force, E_t, is given by the equation

$$E_t = E_j + \frac{RT}{F} \ln \frac{a_{\mathrm{Cl_I}}}{a_{\mathrm{Cl_{II}}}}, \tag{14}$$

where a_{Cl} is the activity of the chloride ion and the subscripts I an II refer, respectively, to the solutions on the left and the right-han members of eq 1. Combination of eq 5 and 14 yields

$$\log \frac{f_{\mathrm{Cl_I}}}{f_{\mathrm{Cl_{II}}}} = \left(\frac{E_t - E_j}{k}\right) - \log \frac{m_{\mathrm{Cl_I}}}{m_{\mathrm{Cl_{II}}}}, \tag{15}$$

where $k = 2.303\ RT/F$ and is equal to 0.05914 at 25° C. All of th quantities to the right of the equality sign in eq 15 are known, an hence the ratio of the activity coefficients of chloride ion in the tw solutions can be obtained from the experimental data. The result are presented in table 5.

The activity coefficients of potassium chloride at 25° C have bee measured by Robinson [19] and by Scatchard, Hamer, and Wood [20 The results have been summarized by Robinson and Harned [21] an yield $f_{\mathrm{KCl}} = 0.592 \pm 0.002$ for the saturated solution. With this valu as a basis, the activity coefficients of chloride in the mixtures may b calculated from the experimental values of $f_{\mathrm{Cl_I}}/f_{\mathrm{Cl_{II}}}$.

Emf measurements of the three cells *AB*, *AC*, and *AD* represen the direct comparison of saturated potassium chloride solution *A* wit the mixtures. The use of $f_{\mathrm{KCl}} = f_{\mathrm{Cl}_A} = 0.592$ for solution *A* yiel values of f_{Cl_B}, f_{Cl_C}, and f_{Cl_D}. For the sake of brevity, these symbo have been shortened to f_A, f_B, f_C, and f_D, respectively. Intercombin tions are thus possible; the quantity f_B, for example, may be combine with the ratios f_B/f_C and with f_B/f_D, obtained from emf measurement on cells *BC* and *BD*, to calculate additional values of f_C and f_D. Th process is repeated for all the nonrecurrent combinations of the si ratios of $f_{\mathrm{Cl_I}}/f_{\mathrm{Cl_{II}}}$ given in table 5. The notation *CD*, *C* for the las entry in table 6, for example, indicates that the ratio of the activit coefficients of the solutions in cell *CD* was combined with the valu of f_C obtained from cell *AC*. The activity coefficients relative t saturated potassium chloride thus obtained are listed in table 6.

TABLE 6.—*Activity coefficient at 25° C of chloride ion in mixtures of concentrated electrolytes containing chloride*

[Basis: f_{KCl}=0.592]

KCl	KCl+KNO_3	KCl+KNO_3+HCl	KCl+HCl
.592	0.5569 (*AB, A*) .5564 (*BC, C*) .5586 (*BD, D*)	0.5590 (*AC, A*) .5595 (*BC, B*) .5601 (*CD, D*)	0.5950 (*AD, A*) .5932 (*BD, B*) .5938 (*CD, C*)
Average	0.5573 ±0.0009	0.5595 ±0.0003	0.5940 ±0.0007

The averages of the values of the activity coefficients of the chloride ion in solutions *B*, *C*, and *D* are, respectively, 0.5573±0.0009, 0.5595 ±0.0003, and 0.5940±0.0007.[8] The deviations from the averages point to an internal consistency of ±0.0007 in the measurement of f, and when combined with an uncertainty of ±0.002 in f_{KCl} yield ±0.003 for the probable errors in the values of f_B, f_C, and f_D compared with saturated potassium chloride.

It is important to note that the addition of potassium nitrate to potassium chloride lowers the relative activity coefficient of the chloride ion (cell *AB*), whereas the opposite effect is observed when hydrochloric acid is added to potassium chloride (cell *AD*) or to potassium chloride containing potassium nitrate (cell *AC*). These observations are in qualitative agreement with the magnitude of the mean activity coefficients at 25° C for separate 4.831-*m* solutions of potassium chloride, 0.592 ±0.002, [21]; potassium nitrate, 0.196 ±0.003, [22] [9]; and of hydrochloric acid, 2.231 ±0.001, [23].

According to Brönsted [24], if two solutions with the same valence type and ionic strength are mixed in the proportions of x to $1-x$, the logarithm of the mean activity coefficient of an electrolyte in the mixture is a linear function of x.[10] In the present work, however, the ionic strength is too high for the successful application of this principle. Treating these cases as an extension of Brönsted's rule would yield f_B=0.439, f_C=0.457 and f_D=0.600. The deviations from the values given in table 6 are considerably greater than the probable experimental errors in the measurements.

The equation

$$\log f_C = \frac{-0.5059C^{1/2}}{1+0.3287a_i C^{1/2}} + 2.2062\times10^{-3}a_i^3 C + 2.6269\times10^{-6}a_i^6 C^2, \quad (16)$$

has been proposed by Van Rysselberghe and Eisenberg [10] for rep-

[8] Uncertainties of ±0.05 percent in concentration and of ±0.02 mv in emf correspond, respectively, to ±0.0005 and ±0.0003 in f. An uncertainty of ±0.02 percent in the equivalent conductance of the ions at infinite dilution alters the calculated value of the potential at the liquid junction by only ±0.002 mv. Because of the assumptions made in the integration of eq 3, especially that regarding the transference numbers at high concentrations, the uncertainties in the absolute values of the liquid junction potentials are unknown. The internal consistency obtained for the values of f_B, f_C, and f_D would indicate, however, that these uncertainties are either small or largely compensated internally by the symmetry of eq 4.

[9] The solubility of potassium nitrate in water at 25° C is given in the International Critical Tables as 3.74 *m*. The value of the activity coefficient at a hypothetical molality of 4.831 was determined by extrapolation.

[10] Güntelberg [25] proved this to be true for solutions 0.1 in ionic strength.

resenting the mean activity coefficient on the molar scale, f_C, of a uni-univalent electrolyte at 25° C in terms of a single parameter a_i and the concentration C in moles per liter of solution. Substitutions of the activity coefficients of individual solutions of potassium chloride [21] potassium nitrate [22], and of hydrochloric acid [23] of the concentration C corresponding to 4.831 m (on the weight basis) into eq 15 yield, respectively, 2.71, 0.91, and 3.79 A for a_i.[11]

The experimental values of log f given in table 6 correspond, respectively, to 2.64, 2 67, and 2.72 A for a_i for solutions B, C, and D. The hydrochloric acid in solution D contributes only 1 percent to the ionic strength of the mixture, and the value of a_i is therefore essentially the same as for pure potassium chloride. These values for a_i lie between those for the constituents of which the mixtures are composed, but they bear neither a linear nor a logarithmic relation to them. The activity coefficients obtained by the assumption of either linear or logarithmic relations are too low by 10 and 20 percent, respectively, and correspond to differences of 0.3 and 0.6 mv in emf, which are much larger than the experimental error.

Equations 10 and 11 on the other hand, yield $f_{HCl}=1.0212$ and $f_{KCl}=0.5940$ for a solution of composition D (in table 1). The latter is identical with the value of f_{Cl} obtained here for the same solution and reported in table 6. It is of interest to note that the value of 0.5940 is the same as obtained by procedure 2b, previously discussed, but many additional measurements on mixtures of hydrochloric acid and potassium chloride are necessary before any conclusions can be drawn regarding the relative merits of the assumptions of MacInnes and Guggenheim.

The method of cells with liquid junctions as employed here is well adapted to measurements of the ratios of the mean activity coefficient of chloride ion in two solutions, especially if the concentrations are high. The best conditions are those in which the liquid junction potentials are small or contribute only a small part to the total emf. The mixtures of electrolytes studied here, or modifications thereof, may be found useful in reference electrodes for the determination of pH by electrometric methods.

V. REFERENCES

[1] R. G. Bates, W. J. Hamer, G. G. Manov, and S. F. Acree, J. Research NBS **29**, 183 (1942) RP1495.
[2] W. J. Hamer and S. F. Acree, J. Research NBS **23,** 647 (1939) RP1261.
[3] G. M. Kline, M. R. Meacham, and S. F. Acree, BS J. Research **8,** 101 (1932) RP403.
[4] M. Planck, Ann. Physik. [3] **39,** 161 (1890); [3] **40,** 561 (1890).
[5] P. Henderson, Z. physik. Chem. **59,** 118 (1907), **63,** 325 (1908).
[6] C. N. Murray and S. F. Acree, BS J. Research **7,** 713 (1931) RP369.
[7] B. Wingfield and S. F. Acree, J. Research NBS **19,** 163 (1937) RP1018.
[8] F. W. Clarke, C. N. Myers, and S. F. Acree, J. Phys. Chem. **20,** 256 (1916).
[9] L. G. Longsworth, J. Am. Chem. Soc. **52,** 1897 (1930).

[11] The value 0.91 A for a_i would appear to be too low for the application of the Debye-Hückel equation [26]. The specific conductance measurements of Robinson and Davies [27] indicate that potassium nitrate is incompletely dissociated at 25° C. Eq 16 does not reproduce the experimental data for the activity coefficients of this salt; the value of a_i varies with the concentration [28].

[10] P. van Rysselberghe and S. Eisenberg, J. Am. Chem. Soc. **62,** 451 (1940).
[11] H. S. Harned, J. Phys. Chem. **30,** 433 (1926).
[12] W. J. Hamer and S. F. Acree, J. Research NBS **17,** 605 (1936) RP930.
[13] W. J. Hamer, Trans. Electrochem. Soc. **72,** 45 (1937).
[14] D. A. MacInnes, Principles of Electrochemistry, (Reinhold Pub. Co., New York, N. Y., 1939).
[15] J. E. Hawkins, J. Am. Chem. Soc. **54,** 4480 (1932).
[16] H. S. Harned, J. Am. Chem. Soc. **57,** 1865 (1935).
[17] D. A. MacInnes, J. Am. Chem. Soc. **41,** 1086 (1919).
[18] E. A. Guggenheim, J. Phys. Chem. **34,** 1758 (1930); J. Am. Chem. Soc. **52,** 1315 (1930).
[19] R. A. Robinson, Trans. Faraday Soc. **35,** 1217 (1939).
[20] G. Scatchard, W. J. Hamer, and S. E. Wood, J. Am. Chem. Soc. **60,** 3061 (1938).
[21] R. A. Robinson and H. S. Harned, Chem. Rev. **28,** 419 (1941).
[22] R. A. Robinson, J. Am. Chem. Soc. **57,** 1165 (1935).
[23] G. Åkerlöf and J. W. Teare, J. Am. Chem. Soc. **59,** 1855 (1937).
[24] N. Brönsted, J. Am. Chem. Soc. **45,** 2898 (1923).
[25] E. Güntelberg, Z. physik. Chem. **123,** 199 (1926).
[26] N. Bjerrum, Kgl. Danske Videnskab. Selskab, Math.-fys. Medd. **7,** No. 9 (1926).
[27] R. A. Robinson and C. W. Davies, J. Chem. Soc. (1938), 574.
[28] P. van Rysselberghe, private communication.

WASHINGTON, May 31, 1944.

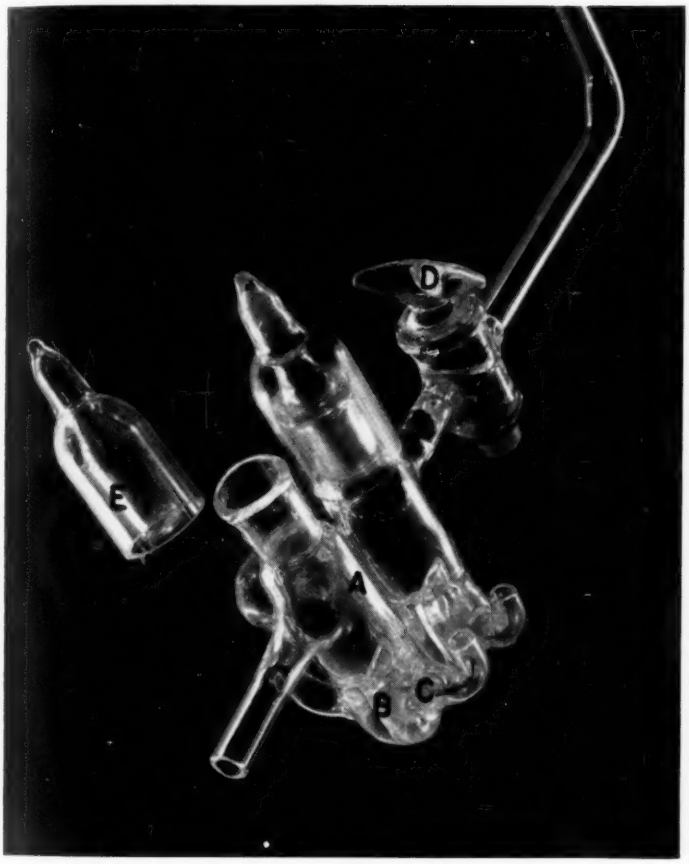

FIGURE 1.—*Calomel half-cells, showing cylinder A, glass partition B, tungsten leads C, stopcock D, and weighted stopper, E.*

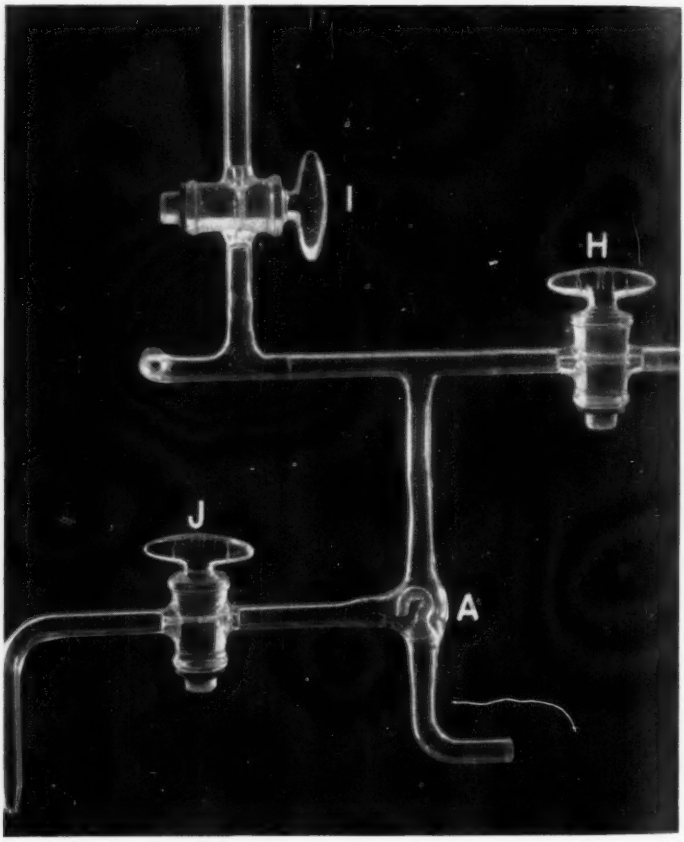

FIGURE 2.—*Details of the liquid junction, A, of the "pig-tail" type.*

See fig. 3 for a description of the functions of stopcocks *H*, *I*, and *J*.

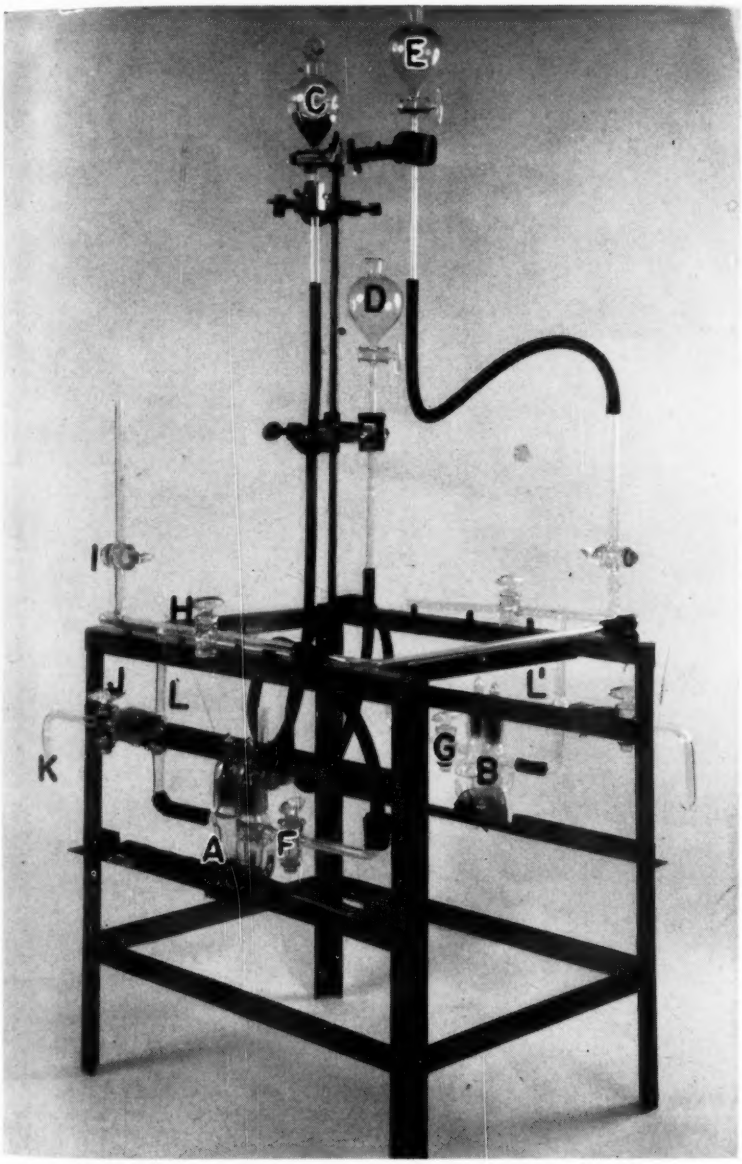

FIGURE 3.—*Liquid-junction and calomel cell assembly, showing half-cells A and B; reservoirs C (for the heavier solution), D and E (for the lighter solution); stopcocks F and G for controlling the rates of flow of the electrolytes to the cells; stopcock H for admitting the lighter solution to the liquid-junction chambers (L or L'), I for removal of entrapped air, and J for discarding the mixed solutions through tip K.*

UNIV. OF MICH.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1609

Part of Journal of Research of the National Bureau of Standards, Volume 33, October 1944

IONIZATION CONSTANT OF BORIC ACID AND THE pH OF CERTAIN BORAX-CHLORIDE BUFFER SOLUTIONS FROM 0° TO 60° C

By George G. Manov, Nicholas J. DeLollis, and S. F. Acree

ABSTRACT

The ionization constant of boric acid was determined by the use of the electromotive force of cells without liquid junctions. Hydrogen and silver–silver-chloride electrodes were immersed in borax-sodium chloride solutions. To reduce the possibility of formation of polyborates, dilute solutions were used. The emf were measured at 5-degree intervals over the temperature range 0° to 60° C.

The negative common logarithm of the ionization constant (pK) of boric acid over the temperature range 0° to 60° C may be represented by the equation

$$pK = 2237.94/T + 0.016883T - 3.305,$$

where T is the absolute temperature.

The data indicate that the mean activity coefficients of the ions of sodium chloride and of sodium borate do not differ appreciably. The pH values for the solutions studied and for rounded values of the concentration are tabulated as functions of temperature and ionic strength. These solutions, which range in pH values from 8.934 to 9.465, can be used as standards in the calibration of glass-calomel and other electrometric pH equipment.

A discussion is given of the significance of the quantity a_i (commonly called the "distance of closest approach" of the ions) and its importance in the calculation of pH values, especially when the buffer ion is not univalent.

The changes in free energy, heat content, entropy, and heat capacity that accompany the ionization of 1 mole of boric acid are listed.

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I. INTRODUCTION

The proper adjustment of the degree of acidity or alkalinity has long been known to be important in the manufacture of many laboratory and commercial products. The control of pH [1] is now a requirement in certain medicinal preparations and in many Federal specifications.

The data reported here form a part of the program for the establishment of pH standards by the National Bureau of Standards. Provisional values for certain buffer solutions have already been published [1].[2]

Very few materials are suitable for use in the standardization of the pH scale in the alkaline range. Borax, $Na_2B_4O_7.10H_2O$, has been frequently used for this purpose, and the pH of solutions of this material, which is approximately 9.2 at 25° C, has been made to cover the range from 8 to 10.5 by the addition of known quantities of acid or base.

The dissociation of tetraborate ion in water to yield simpler ions is well established [2, 3], and measurements of the Raman spectra [3] indicate that the reaction

$$B_4O_7^- + 3H_2O = 2H_3BO_3 + 2BO_2^- \quad (1)$$

is complete. For the purpose of the investigation reported here, it is not important whether the free acid is orthoboric (H_3BO_3) or metaboric (HBO_2), as the concentration of the water in the solutions is not appreciably different. There appears to be some evidence [2] of the formation of tetraboric acid in concentrated solutions, particularly those in which the ratio of free boric acid to borate ion is greater than unity. This view, however, is not upheld by interpretation of the Raman data [3] that have been obtained for various mixtures of borax with hydrochloric acid and for borax with sodium hydroxide in approximately 0.2-*m* solutions. These data indicate that the formation of polyboric acids is probably less than 0.5 percent and that the equations

$$H_3BO_3 + OH^- = BO_2^- + 2H_2O, \quad (2)$$

and

$$H_3BO_3 = H^+ + BO_2^- + H_2O \quad (3)$$

represent the actual course of the reaction [4]. Additional data are needed before accurate pH values can be calculated for solutions which are more acid than those corresponding to equimolal ratios of boric acid and borate ion. A careful study of the freezing points of such acid solutions would help to clarify the picture.

In order to diminish as much as possible the effects of polyborate formation, the experimental measurements reported here were confined to equimolal ratios of boric acid and sodium borate, added as

[1] The term pH is defined as the negative common logarithm of the product of the concentration of hydrogen ion in moles per thousand grams of water and the activity coefficient. Mathematically $pH = -\log_{10}(m_H f_H)$.

[2] Figures in brackets indicate the literature references at the end of this paper.

borax. Likewise, the solutions used were as dilute as practicable, the maximum ionic strength [3] being 0.53.

II. DETERMINATION OF IONIZATION CONSTANTS BY USE OF CELLS WITHOUT LIQUID JUNCTIONS

In the determination of the ionization constant by the use of cells without liquid junctions, hydrogen and silver–silver-chloride electrodes are immersed in the buffer solution containing a known concentration of an alkali chloride. At any given temperature, the "single electrode potential" [4] at the silver–silver-chloride electrode is a function of the known molality of the chloride ion multiplied by the activity coefficient, and the corresponding potential at the hydrogen electrode, at 1-atmosphere pressure of hydrogen, is a function of the activity of the hydrogen ion. Essentially, the total electromotive force of such a galvanic cell depends upon the activity of the chloride ion and the pH of the solution under investigation. As the molality of the chloride ion is known and its activity coefficient may be calculated as shown later, the pH values of the solutions are thus obtained.

The galvanic cell may be represented as follows:

$$Pt|H_2(g, 1\ atm)|H_3BO_3(m_1), NaBO_2(m_2), NaCl(m_3)|AgCl(s)|Ag(s). \quad (4)$$

The symbols have their usual significance. The vertical lines indicate the separation of phases, and the commas set off the different components within the same phase.

When current is drawn from this cell, the reaction is

$$1/2H_2(g, 1\ atm)+AgCl(s)=Ag(s)+H^+ +Cl^-. \quad (5)$$

The electromotive force, the activity coefficients, and the concentrations are related by means of the equation

$$E=E^\circ-\frac{RT}{F}\ln(a_H a_{Cl})=E^\circ-2.30259\frac{RT}{F}\log(a_H m_{Cl} f_{Cl}), \quad (6)$$

in which E is the measured emf, E° the potential of the silver–silver-chloride electrode against the normal hydrogen electrode in a solution of hydrochloric acid at unit activity, and R, T, and F are the gas constant, the absolute temperature, and the value of the Faraday, respectively.

The activity of the hydrogen ion is governed principally by the ionization constant of the buffer acid. The equilibrium constant of the reaction expressed in eq 3 is given by

$$K=\frac{a_H a_{BO_2}}{a_{H_3BO_3}}=\frac{a_H m_{BO_2} f_{BO_2}}{m_{H_3BO_3}}. \quad (7)$$

In eq 7 the assumption is made that the activity of the unionized boric acid is equal to the molality.

[3] The ionic strength is defined as $\mu=1/2\ \Sigma mz^2$, where m is the molality and z is the charge of each ion.
[4] The term is used here merely for convenience.

The hydrolysis of the borate ion causes a small change in the stoichiometric ratio $m_{H_3BO_3}/m_{BO_2}$ by increasing simultaneously the quantity of boric acid and decreasing that of the borate ion. The equations

$$m_{H_3BO_3}=m_1+m_{OH} \tag{8}$$

and

$$m_{BO_2}=m_2-m_{OH}, \tag{9}$$

in which m_1 and m_2 are the stoichiometric molalities of boric acid and of sodium borate, represent the equilibrium concentrations of these two substances in solution. The extent of the hydrolysis varies with the dilution and the temperature. From the values for the ionization constants of boric acid (K) and of water (K_w) and the molality of sodium borate (added as borax), it may be shown that eq 10,

$$m_{H_3BO_3}/m_{BO_2}=1+2K_w/(m_1+2m_{OH})K, \tag{10}$$

is applicable at any temperature. Tabular values of these corrections (table 1) may be interpolated for other temperatures and concentrations. The effect of the activity coefficients is negligible in these corrections.

TABLE 1.—*Values for log* $(m_{H_3BO_3}/m_{BO_2})=\log\ (1+2K_w/(m_1+2m_{OH})K$, *(eq 10)*

Temperature	Concentration of borax in moles per 1,000 g water					
	0.002	0.005	0.010	0.015	0.020	0.025
°C						
0	0.0016	0.0007	0.0003	0.0002	0.0002	0.00
5	.0022	.0009	.0004	.0003	.0002	.00
10	.0030	.0012	.0006	.0004	.0003	.00
15	.0041	.0016	.0008	.0006	.0004	.00
20	.0056	.0023	.0011	.0008	.0006	.00
25	.0074	.0030	.0015	.0010	.0008	.00
30	.0098	.0039	.0020	.0013	.0010	.00
35	.0128	.0052	.0026	.0017	.0013	.00
40	.0167	.0068	.0034	.0023	.0017	.00
45	.0215	.0087	.0044	.0029	.0022	.00
50	.0276	.0113	.0057	.0038	.0029	.00
55	.0351	.0144	.0072	.0048	.0036	.00
60	.0442	.0182	.0092	.0062	.0046	.00

Equations 6 and 7 may be combined to eliminate a_H and yield

$$pK=(E-E^\circ)/k+\log\ (m_{H_3BO_3}/m_{BO_2})+\log m_{Cl}+\log\ (f_{Cl}/f_{BO_2}), \tag{11}$$

where pK equals $-\log K$, and k is written for $2.30259RT/F$.

The values of the quantities in the right-hand member of eq 11 are known except for the term $\log\ (f_{Cl}/f_{BO_2})$. By transposition of the latter, the quantity $pK-\log\ (f_{Cl}/f_{BO_2})=pK'$, the apparent ionization constant, is obtained directly from the experimental data. Extrapolation of the data to zero concentration, at which all activity coefficients are unity, gives the values of pK for each temperature. The values of $pK-pK'$ give the magnitude of $\log\ (f_{Cl}/f_{BO_2})$ but not the activity coefficients of the individual ions.

The activity coefficient of an ion may be represented by any one of several equations, all of which involve certain concepts regarding the electrical field surrounding the ion, the dielectric constant of the medium, and other factors. The original Debye-Hückel expression [5],

$$\log f_i = -Az^2\mu^{1/2}, \tag{12}$$

involves the assumption that the ions behave as point charges. Later, Hückel [6] modified this equation on the supposition that there is a "distance of closest approach", a_i, of ions of opposite charges, and the semithermodynamic equation

$$\log f_i = \frac{-Az^2\mu^{1/2}}{1+Ba_i\mu^{1/2}} + \beta\mu, \tag{13}$$

was thus obtained. In more concentrated solutions or when approximate values of a_i are used [7], the inclusion of the second adjustable parameter β allows eq 13 to represent the experimental data more closely than does eq 12.

The complete expression for the ionization constant of boric acid is obtained by combining eq 11 and 13:

$$pK - \beta^*\mu = (E-E^\circ)/k + \log (m_{H_3BO_3}/m_{BO_2}) + \log m_{Cl} = pK', \tag{14}$$

where pK and pK' are the negative common logarithms of the true and the apparent ionization constants. If all the assumptions made in the derivation of eq 14 are correct, a plot of the three terms to the right of the first equality sign in this equation against ionic strength should yield a straight line, the slope of which is $-\beta^*$. The value of the intercept at zero ionic strength gives pK. The use of eq 6 for computing the pH values and the method of calculating $\log f_{Cl}$ for this case are discussed later.

III. EXPERIMENTAL TECHNIC

I. MATERIALS

All the chemicals used met the American Chemical Society specifications for reagent-grade materials. Borax (decahydrated sodium tetraborate) [5] was recrystallized twice [6] from conductivity water in a large Pyrex flask and the contents protected from atmospheric carbon dioxide by means of tubes containing Ascarite. The crystals on the Büchner funnel were washed once with ice cold conductivity water, twice with ethyl alcohol, and finally twice with ether. The material was then air-dried and bottled. The entire cycle of the washing and drying operations was completed in less than one-half hour after the crystals were first collected. The alcohol and the ether were freshly distilled from quicklime, in order to remove possible traces of acids and nonvolatile products, and were used the same day. This procedure for the preparation of borax containing exactly 10 molecules of water is recommended by Hurley [8].

The water content of several portions of the recrystallized material was determined by fusion of 12-g samples at 900° C to constant weight. An average value of 47.20 ± 0.03 percent was found as compared with

[5] The impurities listed by the manufacturer for this lot totalled 0.003 percent.
[6] The recrystallizations were made below 61° C to avoid formation of the pentahydrate.

the theoretical value of 47.24 percent. Eight months after preparation, analysis showed 47.27 ± 0.02 percent of water and 0.004 percent of carbon dioxide.[7] The alcohol-ether method is satisfactory for the preparation of this material. In addition, it is more convenient than drying moist borax over saturated sodium bromide [9] or saturated sodium chloride and sucrose solutions [10].

The fused borax was prepared in the manner described above, except that the washing with alcohol and ether and the air-drying were omitted. The crystals were warmed as quickly as possible to drive off the free water, and the temperature was then raised above the fusion point of the anhydrous borax. The results in tables 2, 3, and 4, show that both the hydrated and the fused material yield the same value for the ionization constant of boric acid to within an average of 0.0005 unit in pK.

Sodium chloride containing less than 0.01 percent of bromide was further purified by bubbling air through a concentrated, boiling solution of the salt, to which a slight excess of free chlorine had been added. The solution was made slightly acid (pH 5.5), and the bubbling was continued until a negative test for free halogen was obtained on a portion of the solution.[8] Freshly distilled ethyl alcohol was then gradually added to the cooled solution until the concentration of alcohol was approximately 80 percent.[9] The precipitated sodium chloride was filtered by suction, air-dried overnight, heated to 450° C for several hours, cooled, and bottled.

The specific conductance [10] of the water used was 0.8×10^{-6} mho at 25° C. The water was stored in an atmosphere of hydrogen.

Concentrated hydrochloric acid was diluted to correspond to the azeotropic mixture and redistilled in a Pyrex still. The middle third of the distillate was retained.

The hydrogen gas was freed from traces of oxygen by passage over heated palladinized asbestos.

2. SOLUTIONS

Weighted quantities of conductivity water, sodium chloride, and either decahydrated or fused borax were used to prepare accurately 2 liters of stock solution for each series of cell measurements. Proper corrections were made for the water of hydration of the borax. In each case the ionic strength of the stock solution was approximately 0.5. Hydrogen gas was used to force portions of this stock solution into a weight buret, from which known quantities were transferred to each of the 10 dilution flasks, A in figure 1, and the proper amount of conductivity water was added. These solutions were saturated with hydrogen gas and protected at all times from contact with the atmosphere. The weighings were corrected for the mass of hydrogen gas and water vapor in the space above the liquid in the dilution flask.[11] The final solutions contained stoichiometrically equal ratios

[7] The analysis for carbon dioxide was performed by the Detergents, Cements, and Miscellaneous Materials Section of this Bureau.

[8] From the value of the several oxidation potentials involved [11] it should be possible to reduce the total bromide content to 0.001 percent or less.

[9] This fractional precipitation with alcohol has been applied by Hahn [12] for the removal of bromide from potassium chloride.

[10] The conductance measurements were performed by C. G. Malmberg, of the pH Standards Section.

[11] These corrections were of the order of 0.02 percent.

of boric acid to sodium borate (added together as borax) and approximately the same ratio of borate to chloride. The concentration of each component of these solutions was known to within ±0.05 percent. The concentrations, reduced to a vacuum basis, were expressed in moles per 1,000 g of water.

The effect of small quantities of carbon dioxide on the pH of these solutions can be calculated from the approximate ionization constant of boric acid (K_1 [2], and the first and second dissociation constants (K_2 and K_3) of carbonic acid [13] and of water (K_w) [14], together with the activity coefficients of the ions involved.

The equation

$$a_H/f_H + m_{Na} = K_w/a_H f_{OH} + m_1[1 + a_H f_{BO_2}/K_1] + m_2[1 + 2K_3 f_{HCO_3}/a_H f_{CO_3}]/[1 + K_3 f_{HCO_3}/a_H f_{CO_3} + a_H f_{HCO_3}/K_2] \quad (15)$$

represents the equilibrium conditions. m_{Na}, m_1, and m_2 represent, respectively, the total molality of sodium and of all forms of borates and carbonates. The addition of 0.2 mole percent of carbon dioxide to a solution $0.01m$ in borax lowers the pH by 0.002 unit. In view of the small carbonate content found for the recrystallized borax and the precautions taken to exclude contamination by atmospheric carbon dioxide, it is likely that any possible error from this source does not exceed 0.001 pH unit.

3. EQUIPMENT

The water thermostat, potentiometer, and accessory equipment and the method used in making the measurements in this work differ somewhat from a unit described previously [15]. All measurements were performed in a metal-lined constant-temperature room.

Figure 2 is a general view of the water thermostat, some of the cells (A) in position and connected to the hydrogen-supply manifold, the thermoregulator (B), and the cooling coil (C). The cooling coil and expansion valve for the bath are operated in parallel with a similar unit for cooling the room. For temperatures between 0° and 25° C, the diaphragm valve on the refrigerant line is adjusted to cool the bath slightly below the desired temperature, and a small amount of heat is supplied electrically as required.

The temperature of the bath was read by means of a calibrated mercury-in-glass thermometer graduated to 0.2° C, and estimated to 0.02° with the aid of a small magnifier [12]. The uniformity of temperature within the bath was tested with a Beckmann thermometer at 20 different locations, corresponding to the positions of the electrodes when in use. At 0°, 25°, and 60° these deviations from the average temperature were respectively ±0.02°, ±0.01°, and ±0.03°. The variations of the temperatures of solutions inside the cells were approximately one-fifth the above.

The electromotive forces of the galvanic cells were measured in international volts. A precision type of potentiometer, a calibrated standard cell, and a sensitive galvanometer were employed. The emf cells have been described previously [15]. One of these cells, ready to be filled with the buffer solution, is shown in figure 1. The method of filling the cells is described later.

[12] An uncertainty of 0.02° in temperature corresponds to 0.0003 in pH or pK.

4. ELECTRODES

The hydrogen electrodes were constructed from platinum foils 10 by 15 by 0.2 mm, to which were welded short pieces of platinum wire. A glass bead covering part of the wire and both sides of the foil at the weld [13] was fused to a 5-mm glass tube 3 inches long.

The electrodes were cleaned by boiling for 3 minutes in aqua regia (1 part of concentrated nitric acid and 3 parts of concentrated hydrochloric acid) diluted with an equal volume of water. They were first coated electrolytically with a thin layer of gold and then platinized according to the method of Popoff, Kunz, and Snow [16]. The electrodes were usually prepared before each series of determinations (a "run"), although electrodes from a previous run have occasionally been used. No differences larger than 0.02 mv were observed between electrodes freshly prepared, those used in previous runs, and spare electrodes that had been stored in water for a year or more.

The silver–silver-chloride electrodes were of the thermal-electrolytic type [17]. The older electrodes were made by igniting spheroidal masses of silver-oxide paste around platinum-wire spirals and weighed approximately 0.3 g after being chloridized. In the new ones, the silver-oxide paste was pressed within machine-wound platinum spirals 3 mm in diameter by 6 mm long and then ignited and chloridized. The mixture of silver and silver chloride weighed only 0.08 to 0.10 g and was found to reach equilibrium much more rapidly. Aging the electrodes of both forms overnight in a buffer-chloride solution sufficed to bring them to within 0.05 mv of each other. Where equilibrium is reached, they do not differ by more than 0.02 mv from each other after aging for a year or more.

The electrodes were usually prepared several days before each run, and after aging and checking in a dilute chloride solution were stored in distilled water until needed. Three electrodes of one kind, hydrogen or silver–silver-chloride, were mounted in one rubber stopper.[14]

5. PROCEDURE

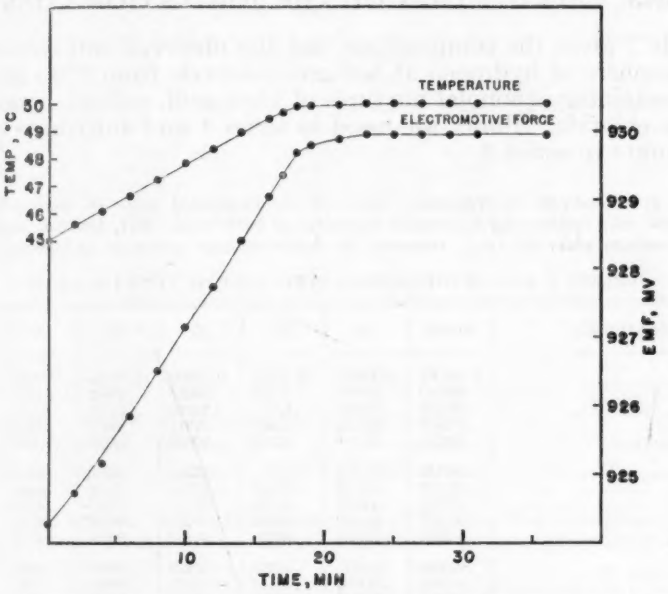
The silver–silver-chloride electrodes were removed from the distilled water in which they had been immersed, dried superficially with filter paper, and soaked overnight in a portion of the proper buffer-chloride solution. When checked the next morning, the electrodes generally agreed to within 0.02 mv. The hydrogen and the silver–silver-chloride electrodes were then placed in the proper cell in which the normal atmosphere had been replaced by hydrogen.

The buffer solution in dilution flask *A* (fig. 1) was forced into the emf cell by means of hydrogen gas, and the stopcocks of the flask were then closed. The solution was expelled from the emf cell through stopcock *B* by means of pressure applied at *C* and the cell refilled. The solution was allowed to stand in the cell approximately 5 minutes before being discarded. This process was repeated three

[13] Soft glass, Pyrex, and "lead sealing-in" glass were found to crack at the bead. Kimble "machine-made flint tubing" has the proper coefficient of expansion for this purpose, and platinum-to-glass seals made from this material will withstand considerable mechanical shock and repeated heatings to 400° C without cracking. Acknowledgment is made to the glassblowing shop of this Bureau for these tests.

[14] The mounting is most conveniently made by thoroughly cooling the rubber stopper in liquid air and drilling the holes in a drill press. The diameter of the drill should be 10 percent less than that of the glass tubing. By this method, a very clean, smooth bore is obtained.

r more times. After the last filling of the cell, solution flask *A* was emoved and a connection to the hydrogen supply was substituted. A slow stream of hydrogen, corresponding to that used in the emf easurements, was passed through saturator bulb *D*, and the slight xcess of solution above the electrodes in the hydrogen-electrode ompartment was run to waste through stopcock *C*. A trap, *E*, as then attached to stopcock *C* and the cell placed in position in he bath (fig. 2) and connected to the hydrogen-supply manifold by eans of a semiflexible copper tubing equipped with brass joints of tandard taper. The silver–silver-chloride and hydrogen electrodes re shown at *F* and *G*.



IGURE 3.—*Typical data of the relation of time and temperature and electromotive force of the cells.*

e bath was heated from 45° to 50° C; the cells reached equilibrium with respect to electromotive force approximately 3 minutes after a new constant temperature in the bath had been attained.

The emf measurements of the 10 cells were first made at 25° C. ecause the solutions were already saturated with hydrogen, equilib- um values for the emf were reached in about 2 hours. The bath as then cooled overnight to nearly 0° C; emf measurements were en made at this temperature and thereafter at 5° intervals up to ° C. After the data had been taken at the highest temperature, e bath was cooled to 25° C and the emf again recorded. In all, ree sets of measurements were made at 25° C. Generally, 3 days ere required to complete the series of measurements. The emf data ere corrected for the vapor pressure of water [18] and to 1 atmosphere hydrogen [19]. Cells whose initial and final emf values at 25° C ffered by more than 0.15 mv (0.0025 pH unit) were rejected as satisfactory.

A study was made of the rapidity with which the temperature and e emf of the cell attained equilibrium when the temperature of the th was raised 5 degrees. The results show that the new thermal

equilibrium in the cell was reached in about 20 minutes, and that there was a lag of only about 3 minutes between the thermal and the electromotive force equilibria. A typical record of the data is shown in figure 3.

The three hydrogen and the three silver–silver-chloride electrodes in the same cell permit nine measurements of the emf. Side reactions and abnormal states of electrodes affecting unequally the emf are revealed quickly. The data from such electrodes were rejected.

IV. ELECTROMOTIVE FORCES OF GALVANIC CELLS CONTAINING BORAX-SODIUM CHLORIDE BUFFER SOLUTIONS; CALCULATION OF THE IONIZATION CONSTANT

Table 2 gives the compositions and the observed emf corrected to 1 atmosphere of hydrogen at 5-degree intervals from 0° to 60° C for cells containing equimolal mixtures of boric acid, sodium borate, and sodium chloride. Borax was used in series 1 and anhydrous sodium tetraborate in series 2.

TABLE 2.—*Observed electromotive force in international volts of hydrogen–silver-chloride cells containing equimolal mixtures of boric acid (m_1), sodium borate (m_2) and sodium chloride (m_3), corrected to 1-atmosphere pressure of hydrogen*

SERIES 1. BORAX (DECAHYDRATED SODIUM TETRABORATE)

Solution No.	$m_1=m_2$	m_3	E_0	E_5	E_{10}	E_{15}	E_{20}
1	0.002906	0.002695	0.89086	0.89607	0.90183	0.90780	0.91
2	.003660	.003394	.88559	.89057	.89637	.90211	.90
3	.005323	.004937	.87701	.88192	.88759	.89328	.89
4	.005963	.005530	.87387	.87911	.88477	.89044	.89
5	.006204	.006106	.87165	.87682	.88239	.88801	.89
6	.007163	.006643	.87001	.87486	.88053	.88610	.89
7	.008830	.008189	.86475	.86988	.87523	.88069	.88
8	.009313	.009165	.86190	.86711	.87247	.87795	.88
9	.011227	.011050	.85763	.86271	.86797	.87337	.87
10	.012767	.011840	.85626	.86137	.86636	.87173	.87
11	.013384	.013171	.85367	.85834	.86374	.86903	.87
12	.016101	.014932	.85101	.85572	.86084	.86607	.87
13	.017902	.017618	.84669	.85170	.85672	.86187	.86
14	.022415	.020788	.84318	.84783	.85278	.85784	.86
15	.026859	.026434	.83754	.84224	.84699	.85192	.85

SERIES 1—Continued

Solution No.	E_{25}	E_{30}	E_{35}	E_{40}	E_{45}	E_{50}	E_{55}	E_{60}
1	0.91955	0.92541	0.93119	0.93705	0.94284	0.94839	0.95386	0.95
2	.91420	.91989	.92572	.93154	.93729	.94308	.94859	.95
3	.90479	.91050	.91616	.92191	.92755	.93320	.93873	.94
4	.90186	.90739	.91306	.91878	.92438	.93003	.93560	.94
5	.89932	.90489	.91057	.91618	.92178	.92732	.93287	.93
6	.89720	.90273	.90829	.91394	.91943	.92507	.93055	.93
7	.89188	.89731	.90279	.90830	.91384	.91941	.92487	.93
8	.88892	.89435	.89988	.90536	.91085	.91655	.92172	.92
9	.88418	.88956	.89507	.90046	.90588	.91131	.91667	.92
10	.88258	.88793	.89333	.89876	.90415	.90960	.91491	.92
11	.87969	.88500	.89044	.89575	.90109	.90643	.91166	.91
12	.87656	.88187	.88712	.89245	.89772	.90308	.90837	.91
13	.87223	.87735	.88265	.88784	.89308	.89835	.90346	.90
14	.86811	.87315	.87832	.88355	.88871	.89397	.89909	.90
15	.86198	.86699	.87192	.87697	.88203	.88707	.89200	.89

TABLE 2.—*Observed electromotive force in international volts of hydrogen-silver-chloride cells containing equimolal mixtures of boric acid (m_1), sodium borate (m_2), and sodium chloride (m_3), corrected to 1-atmosphere pressure of hydrogen*—Con.

SERIES 2. ANHYDROUS SODIUM TETRABORATE

Solution No.	$m_1=m_2$	m_3	E_0	E_5	E_{10}	E_{15}	E_{20}
16	0.003381	0.003403	0.88539	0.89099	0.89666	0.90247	0.90834
17	.005680	.005716	.87308	.87848	.88399	.88964	.89535
18	.007497	.007545	.86659	.87189	.87735	.88289	.88846
19	.009436	.009496	.86128	.86647	.87184	.87719	.88268
20	.009960	.010023	.85992	.86516	.87043	.87582	.88129
21	.014233	.014323	.85158	.85662	.86176	.86693	.87225
22	.015343	.015440	.84987	.85481	.85995	.86516	.87045
23	.018524	.018642	.84553	.85054	.85540	.86061	.86581
24	.020574	.020705	.84322	.84806	.85293	.85809	.86326

SERIES 2—Continued

Solution No.	E_{25}	E_{30}	E_{35}	E_{40}	E_{45}	E_{50}	E_{55}	E_{60}
16	0.91391	0.92013	0.92603	0.93183	0.93760	0.94331	0.94897	0.95428
17	.90083	.90672	.91238	.91799	.92364	.92921	.93475	.94016
18	.89406	.89968	.90529	.91083	.91632	.92186	.92728	.93265
19	.88802	.89363	.89916	.90464	.91011	.91554	.92092	.92629
20	.88671	.89230	.89781	.90325	.90869	.91411	.91953	.92481
21	.87759	.88295	.88828	.89359	.89885	.90415	.90940	.91468
22	.87571	.88099	.88627	.89151	.89675	.90208	.90723	.91233
23	.87103	.87616	.88140	.88661	.89170	.89702	.90214	.90733
24	.86824	.87353	.87868	.88388	.88898	.89416	.89925	.90430

Values of the negative common logarithm of the apparent constant, pK', defined in eq 14, are given in table 3. In calculating these quantities the $E°$ values of Harned and Ehlers [20] were used. Recalculations of $2.30259RT/F$ and of A and B in the Debye-Hückel equation have been made by Manov, Bates, Hamer, and Acree [21].

TABLE 3.—*Values of the negative logarithm of the apparent ionization constant, pK', of boric acid from 0° to 60° C in equimolal mixtures of boric acid, sodium borate, and sodium chloride*

SERIES 1. BORAX

Solution No.	Ionic strength	pK'_0	pK'_5	pK'_{10}	pK'_{15}	pK'_{20}	pK'_{25}
	0.005600	9.5104	9.4331	9.3712	9.3195	9.2709	9.2245
	.007054	9.5132	9.4333	9.3737	9.3195	9.2711	9.2332
	.010260	9.5173	9.4388	9.3795	9.3270	9.2777	9.2356
	.011493	9.5084	9.4371	9.3785	9.3264	9.2782	9.2349
	.012309	9.5105	9.4385	9.3791	9.3268	9.2791	9.2349
	.013805	9.5167	9.4395	9.3825	9.3299	9.2811	9.2354
	.017019	9.5104	9.4401	9.3788	9.3259	9.2787	9.2359
	.018477	9.5067	9.4387	9.3786	9.3268	9.2784	9.2342
	.022277	9.5091	9.4401	9.3795	9.3276	9.2788	9.2354
	.024607	9.5138	9.4457	9.3808	9.3289	9.2796	9.2382
	.026555	9.5123	9.4371	9.3803	9.3279	9.2792	9.2356
	.031032	9.5176	9.4441	9.3832	9.3305	9.2820	9.2370
	.035520	9.5098	9.4431	9.3823	9.3289	9.2794	9.2355
	.043203	9.5168	9.4447	9.3840	9.3301	9.2826	9.2376
	.053293	9.5170	9.4478	9.3840	9.3308	9.2816	9.2378

TABLE 3.—*Values of the negative logarithm of the apparent ionization constant, pK', of boric acid from 0° to 60° C in equimolal mixtures of boric acid, sodium borate, and sodium chloride*—Continued

SERIES 1—Continued

Solution No.	Ionic strength	pK'_{30}	pK'_{35}	pK'_{40}	pK'_{45}	pK'_{50}	pK'_{55}	pK'_{6}
1	.005600	9.1837	9.1465	9.1141	9.0866	9.0584	9.0320	9.00
2	.007054	9.1907	9.1554	9.1232	9.0959	9.0718	9.0464	9.02
3	.010260	9.1954	9.1595	9.1281	9.0999	9.0757	9.0516	9.03
4	.011493	9.1927	9.1575	9.1263	9.0987	9.0744	9.0514	9.02
5	.012309	9.1941	9.1596	9.1272	9.1003	9.0750	9.0521	9.03
6	.013805	9.1943	9.1583	9.1270	9.0990	9.0750	9.0514	9.03
7	.017019	9.1946	9.1585	9.1261	9.0999	9.0762	9.0533	9.03
8	.018477	9.1941	9.1597	9.1275	9.1011	9.0801	9.0532	9.03
9	.022277	9.1953	9.1617	9.1292	9.1028	9.0786	9.0556	9.04
10	.024607	9.1980	9.1630	9.1315	9.1050	9.0813	9.0577	9.05
11	.026555	9.1955	9.1619	9.1293	9.1026	9.0779	9.0538	9.03
12	.031032	9.1976	9.1618	9.1301	9.1031	9.0795	9.0569	9.03
13	.035520	9.1942	9.1604	9.1276	9.1012	9.0772	9.0529	9.03
14	.043203	9.1960	9.1611	9.1299	9.1032	9.0801	9.0563	9.03
15	.053293	9.1978	9.1606	9.1282	9.1015	9.0772	9.0521	9.03

SERIES 2. ANHYDROUS SODIUM TETRABORATE

Solution No.	Ionic strength	pK'_{0}	pK'_{5}	pK'_{10}	pK'_{15}	pK'_{20}	pK'_{2}
16	.006784	9.5108	9.4422	9.3802	9.3272	9.2787	9.23
17	.011397	9.5084	9.4401	9.3798	9.3238	9.2792	9.23
18	.015042	9.5090	9.4411	9.3812	9.3290	9.2808	9.23
19	.018931	9.5107	9.4425	9.3828	9.3289	9.2809	9.23
20	.019982	9.5091	9.4422	9.3811	9.3283	9.2804	9.23
21	.028556	9.5099	9.4423	9.3815	9.3275	9.2797	9.23
22	.030782	9.5111	9.4421	9.3819	9.3292	9.2812	9.23
23	.037166	9.5128	9.4465	9.3825	9.3311	9.2831	9.23
24	.041279	9.5157	9.4470	9.3842	9.3326	9.2849	9.23

SERIES 2—Continued

Solution No.	Ionic strength	pK'_{30}	pK'_{35}	pK'_{40}	pK'_{45}	pK'_{50}	pK'_{55}	pK'_{6}
16	.006784	9.1963	9.1623	9.1299	9.1029	9.0778	9.0550	9.03
17	.011397	9.1962	9.1612	9.1282	9.1018	9.0764	9.0533	9.03
18	.015042	9.1988	9.1645	9.1321	9.1046	9.0800	9.0562	9.04
19	.018931	9.1974	9.1635	9.1313	9.1048	9.0797	9.0563	9.03
20	.019982	9.1988	9.1646	9.1322	9.1055	9.0806	9.0580	9.03
21	.028556	9.1977	9.1628	9.1307	9.1033	9.0785	9.0552	9.03
22	.030782	9.1976	9.1624	9.1296	9.1024	9.0785	9.0541	9.03
23	.037166	9.1989	9.1643	9.1321	9.1037	9.0808	9.0568	9.03
24	.041279	9.2006	9.1653	9.1336	9.1059	9.0815	9.0576	9.04

In figure 4 are plotted the values of the negative logarithm of the apparent ionization constant, pK', for temperatures of 0°, 25°, and 60° C as a function of the ionic strength of the solution. Except at the greatest dilutions, the points at each of the temperatures lie on a straight line within the limits of experimental error. The extrapolation to zero ionic strength was made readily[15] and the values of pK thus obtained.

In table 4 are given the values of pK, K, and β^* at temperatures from 0° to 60° C. At 0°, 25°, and 60° C, calculations were made separately of the pK, K, and β^* values obtained by using borax and anhydrous sodium tetraborate. Table 4 shows that the agreement is well within 0.001 pK unit and that the degree of hydration of the salt is immaterial.

[15] The extrapolation was made by the method of least squares.

TABLE 4.—*Summary of values for* pK, β^*, *and* K *from 0° to 60° C*

Temperature	pK	β^*	$K\times10^{10}$	Remarks [1]
°C				
0	9.5082	−0.17	3.10	Borax.
0	9.5074	.15	3.11	Fused borax.
5	9.4374	.19	3.65	Average value.
10	9.3785	.11	4.18	Do.
15	9.3255	.12	4.73	Do.
20	9.2780	.10	5.27	Do.
25	9.2342	.07	5.83	Borax.
25	9.2337	.16	5.84	Fused borax.
30	9.1947	.07	6.39	Average value.
35	9.1605	.05	6.91	Do.
40	9.1282	.05	7.44	Do.
45	9.1013	.05	7.92	Do.
50	9.0766	.07	8.38	Do.
55	9.0537	.04	8.84	Do.
60	9.0310	.08	9.31	Borax.
60	9.0310	.14	9.31	Fused borax.

[1] The average values for pK, β^*, and K at the temperatures other than 0°, 25°, and 60° C are those for the solutions of borax and of anhydrous sodium tetraborate given in tables 2 and 3, and in figure 4.

In view of the greater ease of preparation, however, it is recommended that borax, prepared as described earlier in this paper, be used instead of the fused material as suggested previously [1].

The equation

$$pK=2237.94/T+0.016883T-3.305, \qquad (16)$$

where T is 273.16 plus the temperature in degrees centigrade, reproduces the experimental variation of pK with absolute temperature to within 0.001 unit[16] except at the two extreme temperatures where

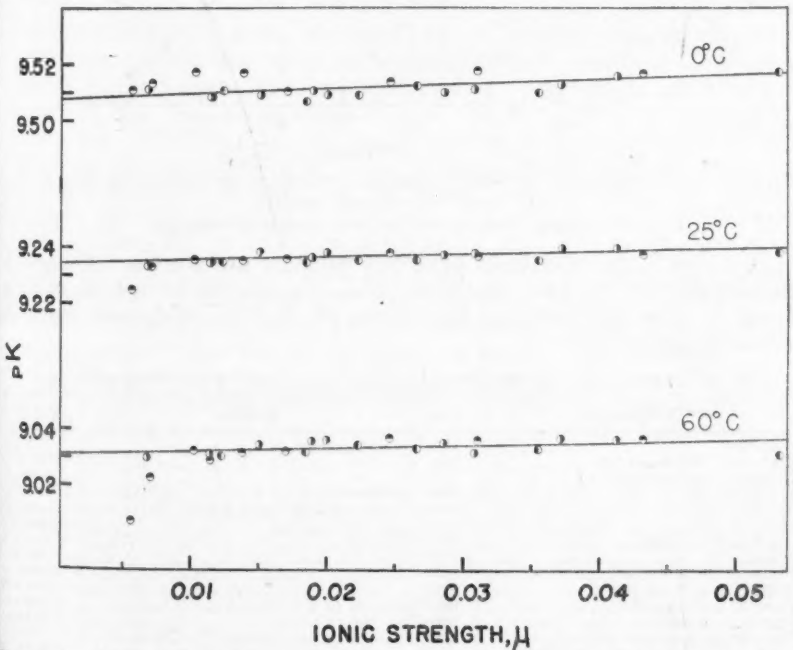


FIGURE 4.—*Plot of the apparent ionization constant,* pK', *versus ionic strength at temperatures of 0°, 25° and 60° C.*

The two series of determinations in which decahydrated borax was used are represented by ◐ and ◓; data for the fused borax are indicated by ◑.

[16] The constants of this equation were obtained by the method of least squares.

the discrepancies are approximately 0.006 unit. The results are expressed graphically in figure 5, where the values of Owen [2] are included for comparison.

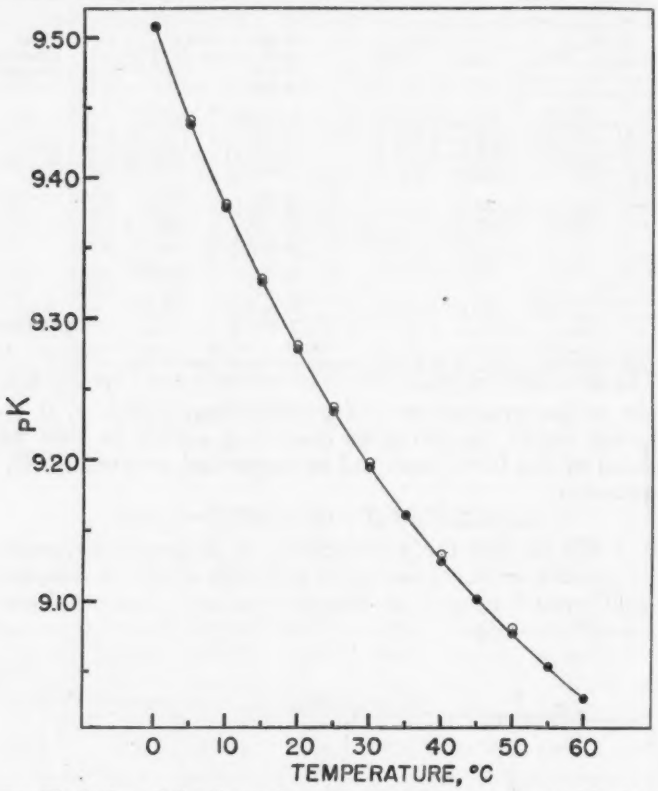


FIGURE 5.—*Variation of the thermodynamic ionization constant of boric acid from 0° to 60° C. (closed circles).*

The open circles represent the data obtained by Owen [2].

In table 5 the results of previous workers are shown. Where the measurements were not made at 25° C, the results have been recalculated to this temperature by values of dpK/dT obtained from the work reported here.

TABLE 5.—*Values of* pK *obtained for boric acid by different workers*

Reference	Year	Method	pK at 25° C
Bock [22]	1887	Conductivity	[a] 9.52
Walker and Cormack [23]	1900	do	[a] 8.71
Hantzsch and Barth [24]	1902	do	8.64
Lundberg [25]	1909	Indicator	[b] 9.19
Sørensen [26]	1909–10	emf (cells with liquid junction)	[a b] 9.19
Pallitzsch [27]	1915	do	[a b] 9.19
Clark and Lubs [28]	1916	do	[a b] 9.08
Menzel [29]	1922	do	[a b] 9.19
Prideaux and Ward [30]	1924	do	[a b] 9.14
Kolthoff and Bosch [31]	1927	do	[a b] 9.13
Fawcett and Acree [32]	1931	do	[a b] 9.13
Hahn and Klockman [33]	1931	do	[a b] 9.10
Britton and Robinson [34]	1932	do	[a b] 9.14
Branch, Yabroff, and Bettman [35]	1934	do	[b] 9.185
Owen [2]	1934	emf (cells without liquid junction)	9.236
This investigation	1943	do	9.234

[a] Values corrected to 25° C by use of dpK/dT obtained from this investigation.
[b] Includes possible errors due to salt effects.

V. pH VALUES OF BORAX-SODIUM CHLORIDE MIXTURES

Equation 6 may be rearranged to give

$$\mathrm{pH}=(E-E^\circ)/k+\log m_{\mathrm{Cl}}+\log f_{\mathrm{Cl}}, \tag{17}$$

from which pH values of the solutions may be calculated when $\log f_{\mathrm{Cl}}$ is known.

In the derivation of eq 13 the parameter a_i was regarded as the sum of the radii of oppositely charged ions in contact. For simple binary salts such a mechanical picture is easily understood, but in more complex solutions each pair of oppositely charged ions can be expected to give rise to different values of a_i. The assumption customarily made is that eq 13 can be applied to each ion of a complex mixture, and for an anion x of charge z, the quantity $\log (f_{\mathrm{Cl}}/f_x)$ is generally expressed by the equation

$$\log (f_{\mathrm{Cl}}/f_x)=\frac{(z^2-1)A\mu^{1/2}}{1+Ba_i\mu^{1/2}}+\beta^*\mu. \tag{18}$$

The use of eq 18 involves the concept that the logarithm of the ratio of activity coefficients can be expressed by the use of "average" values for a_i and for β^*. Under these conditions, the "distance of closest approach" tends to lose its physical significance, and it, as well as the "salt effect term" β^*, become constants whose values are obtained empirically by a process of curve fitting.[17]

When the anion of the buffer acid is univalent, eq 18 reduces to

$$\log (f_{\mathrm{Cl}}/f_x)=\beta^*\mu, \tag{19}$$

in which β^*, as before, is an "average" value for the betas of the two constituents. This use of cells without liquid junctions therefore yields no direct information concerning a_i.[18] The practical solution to this difficulty lies in the experimental determination of the degree of curvature of the plot of pK' as a function of μ (eq 14). A linear relationship will be found only if the values of a_i for the two ions are equal. Examination of the data in figure 4 shows that this condition exists for the solutions studied here. At 0°, 25°, and 60° C the average deviations of the experimental points from linearity are ± 0.0011, ± 0.0009, and ± 0.0014 pK unit, which correspond, respectively, to ± 0.06, ± 0.05, and ± 0.09 mv in emf. These deviations are of the same order of magnitude as the experimental errors and show no significant trend with increasing ionic strength. Calculations indicate that the a_i values for borate and for chloride ions therefore differ by 0.2 A or less, which corresponds to a maximum uncertainty of 0.0008 in pH for the most concentrated solution at the highest temperature.

[17] This concept is strikingly borne out by recent emf measurements made in this laboratory on the second dissociation constant of phenolsulfonic acid [36]. In order to obtain a linear relationship between pK' and μ, it was found necessary to set a_i equal to 8 angstrom units (A), a value considerably higher than the 4 to 5 A found for other acid-salt mixtures [37, 38]. In the calculation of the pH of a solution, an uncertainty may be introduced when this "average" value for a_i is used in eq 13 and 17 in place of the actual value for the chloride ion. Additional experimental work on activity coefficients in mixtures of salts is necessary before improvements can be made in our present methods of calculating pH. The correct value for a_i for use in such cases probably lies between that for hydrochloric acid alone and that which is found necessary to give a linear relationship between pK' and μ. At an ionic strength of 0.05, the difference in the choice between a_i values of 5 and 8. A corresponds to a possible uncertainty of -0.013 unit in the absolute value of the pH. At present there are no adequate theoretical methods for calculating the magnitude of these effects.

[18] This situation applies to all buffer acids (or bases) in which only the first ionization constant is involved, regardless of the number of species derivable by further ionization. For multivalent anions, values of a_i (and of β) are obtainable from the experimental data and apply only to the particular mixture studied. The assumption is generally made, however, that the a_i values for the uni- and the bivalent ions of the same acid are equal.

Accurate measurements of the activity coefficients of sodium chloride solutions from 15° to 45° C are available from the recent work of Janz and Gordon [39]. The numerical values obtained for a_i by these authors have been recalculated [19] to conform to the preferred values of A and B [21] and are 4.4, 4.4, 4.4, and 4.3 A, respectively, at 15°, 25°, 35°, and 45° C. The average, 4.4 A, has been used here to calculate the pH of borax-sodium chloride buffer soutions from 0° to 60° C.[20]

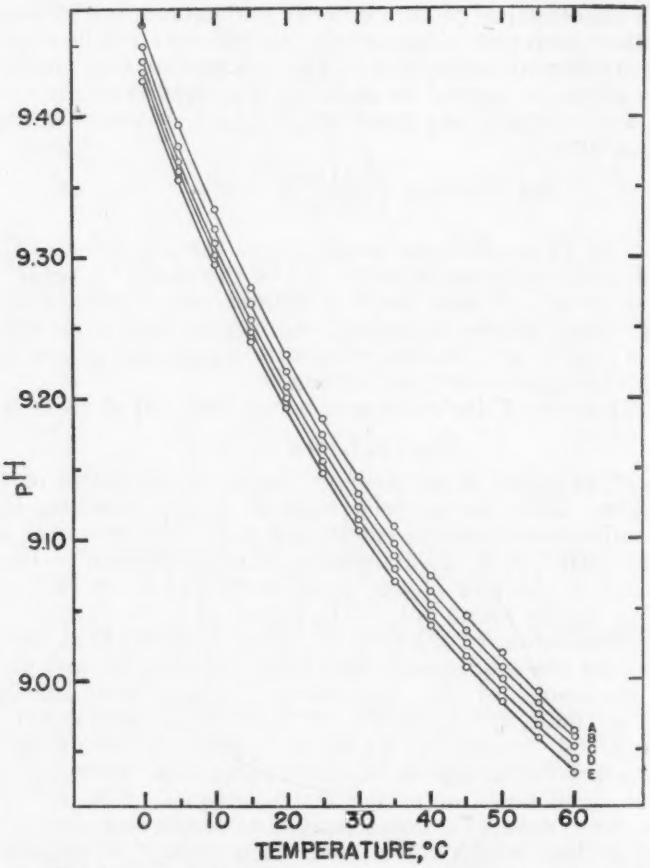


FIGURE 6.—pH *values of equimolal mixtures of boric acid, sodium borate, and sodium chloride from 0° to 60° C at ionic strengths of 0.01 (A), 0.02 (B), 0.03 (C), 0.04 (D), and 0.05 (E), respectively.*

In table 6 the pH values are given for the solutions in series 1 and 2, arranged in order of increasing ionic strength. The pH values from

[19] The quantities A, B, a_i and β must be self-consistent in order to express correctly the experimentally determined values of the activity coefficients.

[20] Although the a_i values for the chloride and borate ions in this mixture are equal, there is a possible objection to the assumption that the a_i for the mixture is the same as that for pure sodium chloride. Consideration of the work of Güntelberg [40], Hawkins [41], Harned [42], and others on the activity coefficients of mixtures indicates that the above objection is not serious and is unlikely to give rise to uncertainties exceeding 0.002 pH unit.

)° to 60° C at integral ionic strengths are given in table 7 and are presented graphically in figure 6. The values in both tables are regarded as accurate to 0.003 pH unit.

TABLE 6.—pH *values of borax-sodium chloride mixtures from 0° to 60° C*

Solution No.	Ionic strength	0°	5°	10°	15°	20°	25°
	0.006784	9.473	9.404	9.341	9.287	9.238	9.192
	.011397	9.461	9.392	9.331	9.275	9.230	9.185
	.011493	9.461	9.389	9.330	9.277	9.229	9.184
	.012309	9.461	9.389	9.329	9.276	9.228	9.183
	.013805	9.465	9.387	9.330	9.277	9.228	9.181
	.015042	9.455	9.387	9.327	9.274	9.226	9.182
	.017019	9.454	9.383	9.322	9.268	9.221	9.177
	.018477	9.448	9.379	9.320	9.267	9.218	9.173
	.018931	9.451	9.382	9.323	9.269	9.220	9.175
	.019982	9.448	9.380	9.320	9.267	9.218	9.175
	.022277	9.445	9.375	9.316	9.263	9.214	9.170
	.024607	9.447	9.378	9.314	9.262	9.212	9.170
	.026555	9.443	9.367	9.312	9.258	9.210	9.165
	.028556	9.439	9.370	9.311	9.256	9.208	9.165
	.030782	9.438	9.367	9.309	9.255	9.207	9.163
	.031032	9.444	9.369	9.310	9.256	9.208	9.162
	.035520	9.432	9.364	9.305	9.250	9.201	9.156
	.037166	9.433	9.365	9.304	9.251	9.203	9.159
	.041279	9.432	9.362	9.302	9.249	9.201	9.156
	.043203	9.432	9.358	9.300	9.245	9.198	9.152
	.053293	9.424	9.353	9.292	9.238	9.189	9.145

Solution No.	Ionic strength	30°	35°	40°	45°	50°	55°	60°
	0.006784	9.152	9.116	9.081	9.051	9.022	8.994	8.964
	.011397	9.145	9.108	9.073	9.045	9.017	8.990	8.964
	.011493	9.141	9.105	9.072	9.042	9.015	8.989	8.962
	.012309	9.141	9.105	9.071	9.042	9.014	8.989	8.963
	.013805	9.139	9.102	9.069	9.039	9.013	8.987	8.963
	.015042	9.142	9.106	9.073	9.043	9.016	8.990	8.965
	.017019	9.135	9.098	9.064	9.036	9.010	8.985	8.961
	.018477	9.132	9.097	9.064	9.036	9.012	8.984	8.959
	.018931	9.135	9.101	9.067	9.039	9.011	8.986	8.962
	.019982	9.135	9.100	9.067	9.038	9.011	8.987	8.962
	.022277	9.129	9.095	9.061	9.033	9.007	8.982	8.958
	.024607	9.129	9.094	9.061	9.033	9.007	8.982	8.958
	.026555	9.125	9.091	9.057	9.029	9.002	8.977	8.952
	.028556	9.125	9.090	9.056	9.027	9.000	8.976	8.953
	.030782	9.122	9.087	9.053	9.024	8.998	8.973	8.947
	.031032	9.122	9.086	9.053	9.025	8.999	8.976	8.951
	.035520	9.115	9.081	9.047	9.019	8.993	8.968	8.944
	.037166	9.118	9.083	9.050	9.020	8.995	8.971	8.947
	.041279	9.116	9.081	9.048	9.019	8.993	8.968	8.943
	.043203	9.110	9.075	9.043	9.015	8.990	8.966	8.942
	.053293	9.105	9.068	9.034	9.006	8.980	8.955	8.930

TABLE 7.—pH *values of borax-sodium chloride buffers at rounded values of the ionic strength*

Temperature	Ionic strength				
	0.01	0.02	0.03	0.04	0.05
°C					
0	9.465	9.449	9.439	9.431	9.425
5	9.394	9.379	9.368	9.361	9.355
10	9.334	9.320	9.310	9.302	9.296
15	9.278	9.267	9.256	9.247	9.240
20	9.231	9.219	9.208	9.200	9.193
25	9.185	9.174	9.164	9.155	9.147
30	9.144	9.132	9.123	9.114	9.106
35	9.109	9.097	9.088	9.079	9.070
40	9.073	9.063	9.054	9.046	9.039
45	9.046	9.035	9.026	9.017	9.009
50	9.019	9.009	9.001	8.993	8.985
55	8.992	8.984	8.976	8.968	8.959
60	8.964	8.960	8.953	8.944	8.934

Each of the solutions in table 7 may be used as a pH standard. An error of 1 percent in the total concentration corresponds to less than 0.001 in pH, and it is therefore permissible to make up the solution to a total volume of 1 liter instead of weighing out the water separately. A solution composed of 0.01 mole (3.814 g) borax and 0.02 mole (1.169 g) sodium chloride per liter of solution is readily prepared and has a pH of 9.155 at 25° C.

Electrometric pH equipment such as glass-calomel and hydrogen-calomel assemblies and special glass electrodes for determining the pH of highly alkaline materials may be calibrated by means of these solutions. During the past 2 years several hundred comparisons have been made between the pH of a 0.05–*m* solution of potassium acid phthalate (NBS Standard Sample 84 a) and borax-chloride solutions, using various commercial vacuum-tube pH meters. In practically all cases the calibrations of the meter with phthalate and with borax, performed by using these two standards in either order, agreed to within 0.01 pH unit, the limit of error of the best instrument. However, if the glass electrode was old or had been mishandled, the pH-emf relationship departed from linearity, and the agreement between the calibrations then differed by as much as 0.06 unit.

VI. RELATED THERMODYNAMIC QUANTITIES

Values expressed in international joules of the changes in free energy, entropy, heat content, and heat capacity which accompany the ionization of 1 mole of boric acid at infinite dilution [21] can be computed from the following general equations [43], together with the appropriate numerical values from eq 16:

[21] In accordance with the convention regarding the hydration of solutes at infinite dilution [43], the respective values for orthoboric and metaboric acid are identical.

$$\Delta F^\circ = -RT \ln K = 2.30259 RT pK = 42836 + 0.32315 T^2 - 63.264 T \quad (20)$$
$$\Delta S^\circ = -(\partial \Delta F^\circ / \partial T)_P = -0.64631 T + 63.3 \quad (21)$$
$$\Delta H^\circ = \Delta F^\circ + T\Delta S^\circ = 42836 - 0.32315 T^2 \quad (22)$$
$$\Delta C^\circ_P = (\partial \Delta H^\circ / \partial T)_P = -0.64631 T \quad (23)$$

The value of R used throughout this paper is that of Cragoe [44]; 8.3127 int. j deg^{-1}. For comparison with data in the literature, the calorie is taken equal to 4.1833 int. j [45]. The derived thermodynamic quantities are given in table 8.

TABLE 8.—*Derived thermodynamic quantities for the process:* $H_3BO_3(aq) = H^+(aq) + BO_2^-(aq)$

Temperature	ΔF°		ΔF°		ΔF°		ΔF°	
°C	*Int. j*	*cal*	*Int. j*	*cal*	*Int. j*	*cal*	*Int. j*	*cal*
0	49,667	11,873	18,723	4,476	−113.3	−27.1	−176.5	−42.2
5	50,242	12,010	17,833	4,263	−116.5	−27.9	−179.8	−43.0
10	50,832	12,151	16,926	4,046	−119.7	−28.6	−183.0	−43.7
15	51,439	12,296	16,002	3,825	−122.9	−29.4	−186.2	−44.5
20	52,062	12,445	15,063	3,601	−126.2	−30.2	−189.5	−45.3
25	52,701	12,598	14,107	3,372	−129.4	−30.9	−192.7	−46.1
30	53,356	12,755	13,136	3,140	−132.7	−31.7	−195.9	−46.8
35	54,028	12,915	12,148	2,904	−135.9	−32.5	−199.2	−47.6
40	54,715	13,079	11,144	2,664	−139.1	−33.3	−202.4	−48.4
45	55,419	13,248	10,124	2,420	−142.4	−34.0	−205.6	−49.2
50	56,139	13,420	9,088	2,172	−145.6	−34.8	−208.9	−49.9
55	56,875	13,596	8,036	1,921	−148.8	−35.6	−212.1	−50.7
60	57,627	13,775	6,967	1,665	−152.1	−36.3	−215.3	−51.5

VII. REFERENCES

[1] R. G. Bates, W. J. Hamer, G. G. Manov, and S. F. Acree, J. Research NBS **29**, 183 (1942) RP1495.
[2] B. B. Owen, J. Am. Chem. Soc. **56**, 1695 (1934); **57**, 1526 (1935).
[3] J. H. Hibben, The Raman Effect, (ACS Monograph No. 80 (Reinhold Publishing Co., New York, N. Y., 1939)).
[4] J. H. Hibben, private communication.
[5] P. Debye and E. Hückel, Physik. Z. **24**, 185, 305, 334 (1923).
[6] E. Hückel, Physik. Z. **26**, 93 (1925).
[7] E. A. Guggenheim, Phil. Mag. **22** [12] 322 (1936).
[8] F. H. Hurley, Ind. Eng. Chem., Anal. Ed. **8**, 220 (1936); **9**, 237 (1937).
[9] I. M. Kolthoff, J. Am. Chem. Soc. **48**, 1447 (1926).
[10] H. Menzel, Z. anorg. allgem. Chem. **224**, 10 (1935).
[11] W. M. Latimer, The Oxidation States of the Elements and Their Potentials in Aqueous Solutions (Prentice-Hall, Inc., New York, N. Y., 1938).
[12] F. L. Hahn, J. Am. Chem. Soc. **57**, 2537 (1935).
[13] D. A. MacInnes and D. Belcher, J. Am. Chem. Soc. **55**, 2630 (1933); **57**, 1683 (1935).
[14] H. S. Harned and W. J. Hamer, J. Am. Chem. Soc. **55**, 2194 (1933).
[15] R. G. Bates and S. F. Acree, J. Research NBS **30**, 129 (1943) RP1524.
[16] S. Popoff, A. H. Kunz, and R. D. Snow, J. Phys. Chem. **32**, 1056 (1928).
[17] E. R. Smith and J. K. Taylor, J. Research NBS **20**, 837 (1938) RP1108; **22**, 307 (1939) RP1183.
[18] N. S. Osborne, H. F. Stimson, and D. C. Ginnings, J. Research NBS **23**, 261 (1939) RP1229.
[19] N. E. Loomis and S. F. Acree, J. Am. Chem. Soc. **38**, 2391 (1916).
[20] H. S. Harned and R. W. Ehlers, J. Am. Chem. Soc. **55**, 2179 (1933).
[21] G. G. Manov, R. G. Bates, W. J. Hamer, and S. F. Acree, J. Am. Chem. Soc. **65**, 1765 (1943).
[22] O. Bock, Ann. Physik. **266**, 638 (1887).
[23] J. Walker and W. Cormack, J. Chem. Soc. **77**, 5 (1900).

[24] A. Hantzsch and A. Barth, Ber. dent. Chem. Ges. **35,** 216 (1902).
[25] J. Lundberg, Z. physiol. Chem. **69,** 442 (1909).
[26] S. P. L. Sørensen, Biochem. Z. **21,** 131, 201 (1909); **22,** 352 (1910).
[27] S. Palitzsch, Biochem. Z. **70,** 333 (1915).
[28] W. M. Clark and H. A. Lubs, J. Biol. Chem. **25,** 479 (1916).
[29] H. Menzel, Z. physik. Chem. **100,** 276 (1922).
[30] E. B. R. Prideaux and A. T. Ward, J. Chem. Soc. **125,** 69 (1924).
[31] I. M. Kolthoff and M. Bosch, Rec. trav. Chim. **46,** 180 (1927).
[32] E. H. Fawcett and S. F. Acree BS J. Research **6,** 757 (1931) RP302.
[33] F. L. Hahn and R. Klockmann, Z. physik. Chem. **35,** 1433 (1931).
[34] H. T. S. Britton and R. A. Robinson, Trans. Faraday Soc. **28,** 531 (1932).
[35] G. E. K. Branch, D. L. Yabroff, and B. Bettman, J. Am. Chem. Soc. 56 937 (1934).
[36] R. G. Bates and S. F. Acree, J. Research NBS **31,** 205 (1943) RP1559.
[37] W. J. Hamer and S. F. Acree, J. Research NBS **24,** 269 (1940) RP1284; W. J. Hamer, J. O. Burton, and S. F. Acree, J. Research NBS **24,** 2[illegible] (1940) RP1289.
[38] R. G. Bates and S. F. Acree, J. Research NBS **30,** 129 (1943) RP1524.
[39] G. J. Janz and A. R. Gordon, J. Am. Chem. Soc. **65,** 218 (1943).
[40] E. Güntelberg, Z. physik. Chem. **123,** 199 (1926).
[41] J. E. Hawkins, J. Am. Chem. Soc. **54,** 4480 (1932).
[42] H. S. Harned, J. Am. Chem. Soc. **57,** 1865 (1935).
[43] G. N. Lewis and M. Randall, Thermodynamics and the Free Energy of Chemical Substances (McGraw-Hill Book Co., Inc., New York, N. Y., 1923).
[44] C. S. Cragoe, J. Research NBS **26,** 495 (1941) RP1393.
[45] Premier Rapport de la Commission Permanente de Thermochemie, International Union of Chemistry, p. 3 (1934); F. D. Rossini, Chem. Rev. **27,** 1 (1940).

WASHINGTON, June 20, 1944.

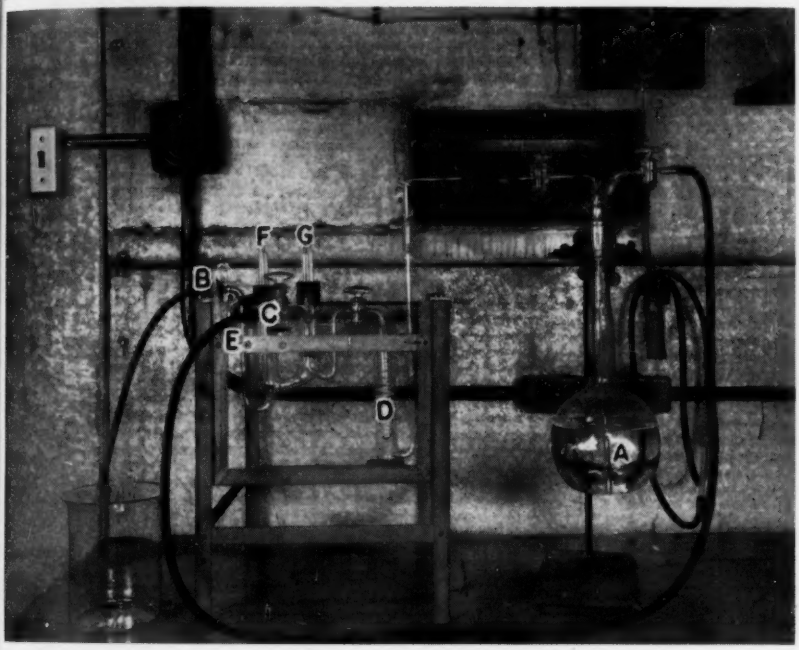


FIGURE 1.—*Electromotive force cell in position for filling, showing solution flask A, overflow stopcocks B and C, saturator D, trap E, and electrodes F and G.*

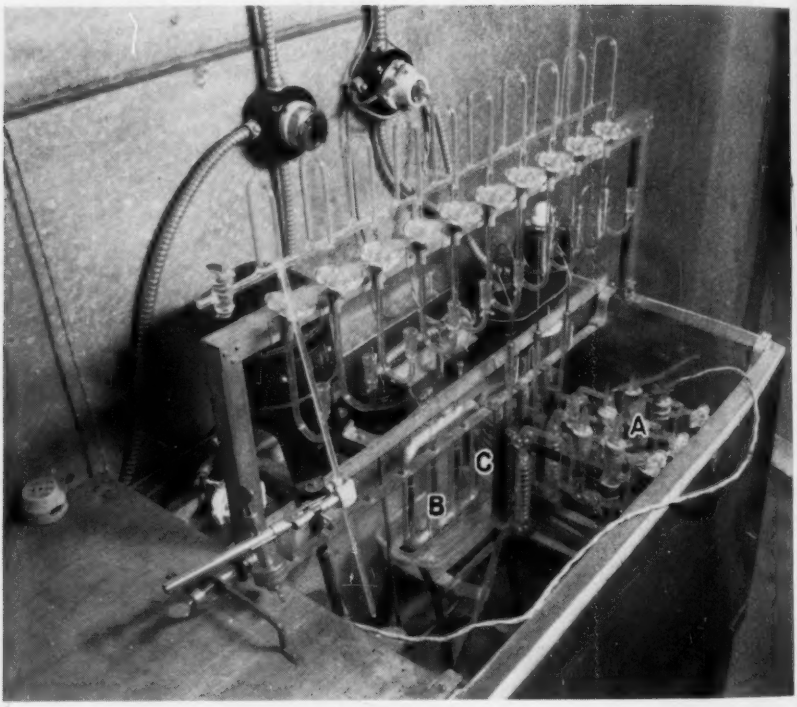


FIGURE 2.—*General view of the bath, showing electromotive force cells, A, connected to the hydrogen-supply manifold by means of the semiflexible copper tubing, the thermoregulator B, and the cooling coil, C.*

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1610

Part of Journal of Research of the National Bureau of Standards, Volume 33, October 1944

DETERMINATION OF TIN IN NONFERROUS METALS BY DISTILLATION AS BROMIDE AND PRECIPITATION WITH CUPFERRON

By William D. Mogerman

ABSTRACT

A gravimetric method is described for the determination of tin in copper-base and lead-base alloys. The procedure involves separation of the tin by distillation, precipitation with cupferron, and ignition to stannic oxide. Results obtained by applying the method to known amounts of tin and to a number of nonferrous alloys show that an accuracy to ±0.2 mg can be expected for amounts of tin ranging from 0.05 to 0.24 g.

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I. INTRODUCTION

In the analysis of nonferrous alloys, tin is usually determined by titration of stannous chloride with an iodine or iodate solution. The reduction of tin to stannous chloride is effected in acid solution by means of a metal. Lead, nickel, aluminum, antimony, and iron have been used for this purpose. The method is subject to certain limitations, which have been discussed frequently in the literature. Molybdenum [1] * and vanadium [1] are partially reduced and cause high results. Tungsten [1] interferes by reason of its color. Copper [2], antimony [2], arsenic [3], iron [3], titanium [4], and potassium iodide [4] have been stated to interfere under certain conditions. In order to overcome the effect of these impurities, Scherrer [5] separated the tin by distilling as stannic tetrabromide prior to reduction and titration.

It has been claimed that oxygen [4] dissolved in the oxidizing reagent also causes erroneous results. When an iodine solution

*Figures in brackets indicate the literature references at the end of this paper.

is standardized with tin, the titer of the solution is slightly higher than that obtained by standardization with arsenious oxide. This effect is apparently not directly proportional to the oxygen concentration, hence it is impractical to compensate for it by adjusting the blank correction. To decrease this oxygen error, it has been recommended that potassium iodate [3] be used instead of iodine. An apparatus [4] designed to prepare oxygen-free iodine solutions has been recommended, but this apparatus does not appear to be convenient for everyday use. It is evident that the iodometric method for the determination of tin is subject to limitations in work of high accuracy, although the errors involved may be small and not prohibitive for most commercial work.

Kling and Lassieur [6] first proposed the use of cupferron for the quantitative determination of tin in the hydrofluoric acid filtrate obtained after separation of antimonous sulfide by the method described by McCay [7]. The cupferron is added in the presence of a large excess of boric acid, used to form a slightly dissociated complex with the free hydrofluoric acid present. The tin-cupferron compound is ignited to stannic oxide. Subsequently these authors stated that for rapid work they preferred an electrolytic method for tin.

Furman [8] also studied this combination of the McCay method with the cupferron precipitation of tin, and separated tin from antimony, zinc, manganese, cobalt, and nickel. The use of hydrofluoric acid is an obvious disadvantage of this method.

Pinkus and Claessens [9] precipitated tin with cupferron in the presence of antimony, arsenic, and zinc. This separation requires that antimony be in the quinquevalent state. The valences of the tin and arsenic are immaterial.

In the proposed method the sample is decomposed with nitric acid[1] and the tin separated as impure stannic oxide. This precipitate, which contains in the usual case all the arsenic and antimony, is dissolved in nitric and sulfuric acids, and the solution treated with hydrazine sulfate to reduce the arsenic and antimony to the trivalent state. The solution is transferred to a distilling apparatus, and the arsenic and the bulk of the antimony removed by distillation, phosphoric acid having been added to retain the tin. The tin is now distilled into a separate receiver by the use of diluted hydrobromic acid, and the distillate treated with potassium permanganate to oxidize traces of antimony. After proper adjustment of the acidity, tin is precipitated with cupferron, filtered, and ignited to stannic oxide.

II. PROCEDURE FOR COPPER-BASE AND LEAD-BASE ALLOYS

1. DISTILLING APPARATUS

An all-glass distilling apparatus, similar to that designed by Scherrer [5] was used in this work. Small modifications were made as to size and compactness.

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[1] Throughout this paper whenever acids are mentioned, nitric acid will refer to the concentrated acid of sp gr 1.42; sulfuric acid, the concentrated acid of sp gr 1.84; phosphoric acid, the acid containing 85 percent of H_3PO_4; and hydrobromic acid, the acid containing 48 percent of HBr. Diluted acids will be designated as follows: For example, diluted nitric acid (1+2) will mean 1 part of nitric acid diluted with 2 parts of water.

In figure 1, *A* is a constricted tube having a capacity of about 60 ml. All solutions are added through this tube. It is sealed to a stopcock having a straight 3-mm bore. The tube extending from *A* into *B* has a diameter of not over 4-mm in order to maintain a column of liquid in it. The side tube in *B* is for the purpose of introducing a stream of carbon dioxide. *B* is sealed to the top of the flask neck, and should

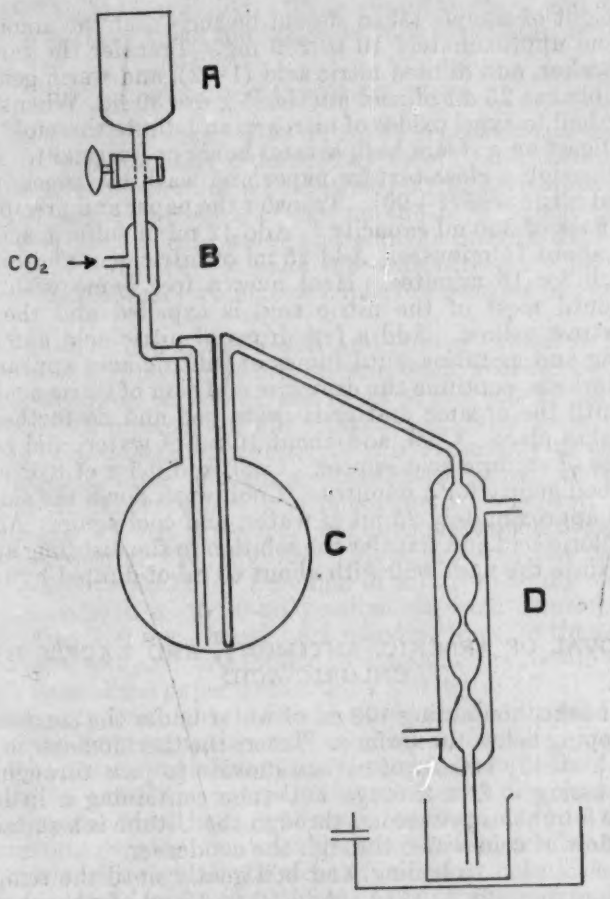

FIGURE 1.—*Distilling apparatus.*

extend as close to the bottom (without touching) as possible, say 1 to 2 mm. This is to minimize bumping.

The boiling flask, *C*, has a capacity of 1,000 ml. It is provided with a delivery tube leading to a condenser, and a thermometer-well closed at the bottom. The thermometer-well is sealed to the top of the flask neck, and reaches nearly to the bottom of the flask. The distance between the bottom of the flask and the delivery tube is 16 to 17 cm. The flask, *C*, rests on an asbestos board having a round hole about 4 cm in diameter to receive the burner flame. The apparatus is fastened to a large ring stand by a clamp at *D*.

The distillate is collected in a beaker containing 100 ml of cold distilled water so placed that the tip of condenser *D* is slightly immersed. An evaporating dish with a side exit tube is provided to hold the beaker and also to catch the condenser water which is permitted to flow into it.

2. PREPARATION OF THE SOLUTION

The weight of sample taken should be such that the amount of tin ranges from approximately 10 to 200 mg. Transfer the sample to a covered beaker, add diluted nitric acid (1+2), and warm gently. For a 1-g sample use 25 ml of acid and for 5 g use 80 ml. When solution is complete, boil to expel oxides of nitrogen and dilute threefold with hot water. Digest on a steam bath several hours or overnight. Filter the solution through a close-texture paper and wash the precipitate with hot diluted nitric acid (1+99). Transfer the paper and precipitate to a Kjeldahl flask of 300 ml capacity.[2] Add 12 ml of sulfuric acid and let stand for about 15 minutes. Add 25 ml of nitric acid and digest on a steam bath for 15 minutes. Heat over a free flame with constant rotation until most of the nitric acid is expelled and the solution becomes straw yellow. Add a few drops of nitric acid and continue the heating and agitation until fumes of sulfuric acid appear. If the solution darkens, continue the dropwise addition of nitric acid and the heating until the organic matter is destroyed and no further change of color takes place. Cool, add about 10 ml of water, and evaporate until fumes of sulfuric acid appear. Cool, add 0.5 g of hydrazine sulfate, and boil gently for 5 minutes.[3] Cool, wash down the sides of the flask with approximately 25 ml of water, and cool again. Add 10 ml of hydrochloric acid and transfer the solution to the distilling apparatus (fig. 1). Rinse the flask well with about 80 ml of diluted hydrochloric acid (1+1).

3. REMOVAL OF ARSENIC, ANTIMONY, AND EXCESS HYDROCHLORIC ACID

Place a beaker containing 100 ml of water under the condenser with the end dipping below the surface. Insert the thermometer in the well and allow a steady stream of carbon dioxide to pass through the apparatus, passing it first through a U-tube containing a little water. About 2 to 3 bubbles per second through the U-tube is a suitable rate. Start the flow of cold water through the condenser.

Heat the solution to boiling, and boil gently until the temperature rises to approximately 110° C. Add 10 to 12 ml of phosphoric acid, and increase the rate of heating. When the temperature reaches 155° C, add 25 ml of hydrochloric acid [4] dropwise at a rate of 30 to 40 drops per minute, maintaining the temperature at 160°±5° C. Discontinue the heating, lower the receiver, and rinse the condenser tip.

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[2] Some copper-base alloys contain an appreciable amount of iron, which exerts a solvent action on metastannic acid. In analysis of the highest accuracy, or if more than 5 mg of iron is present, the dissolved tin must be recovered. Add diluted ammonium hydroxide (1+1) to the filtrate until it is strongly alkaline, boil, filter, wash with diluted ammonium hydroxide (1+10), and finally with water. Add the paper and precipitate to the Kjeldahl flask containing the first precipitate.

[3] This step, intended to reduce arsenic and antimony, is necessary for separation of these elements by volatilization. However, if they are known to be absent or very low in amount the operation can be omitted.

[4] This amount of hydrochloric acid will usually suffice to remove the most of any antimony present. Complete removal requires considerably more hydrochloric acid and is not essential.

4. DISTILLATION OF TIN

Allow the solution in *C* to cool to about 150° C and place in position a new receiver containing 100 ml of water. Transfer hydrobromic acid mixture [5] to *A*, and allow it to drop into *C* at a rate of 30 to 40 drops per minute. Resume distillation [6] by raising the temperature quickly to 180° C. Maintain the temperature between 180° and 185° C until all the acid has been added. Then cut off the heat and the flow of carbon dioxide, and rinse the inside as well as outside of the condenser tip.[7]

5. PRECIPITATION OF TIN

Dilute [8] the distillate with water until the concentration of hydrobromic acid is approximately 6 percent by volume and then add 1 *N* potassium permanganate solution dropwise and with vigorous stirring until an amber color appears. Shake up the filter paper, that was used as a cover, with a little water and add the pulp to the solution. Add sufficient sulfuric acid to make the concentration 4 percent by volume after the necessary volume of cupferron solution has also been added.

Chill the solution in ice water and add chilled cupferron solution (6 g per 100 ml of water) in a slow stream, while stirring vigorously. For amounts of tin up to 10 mg, use 10 ml of reagent, for 50 mg use 40 ml, and for 200 mg use 110 ml. Avoid a large excess of reagent. Precipitation is complete immediately. Stir vigorously to coagulate the precipitate and filter through a close-texture paper containing a small amount of paper pulp. It is important to wash out halogen acids completely. Wash the paper and precipitate thoroughly with cold diluted cupferron wash solution (25 ml of 6-percent cupferron solution diluted to 1,000 ml). Amounts of tin up to 80 mg should be washed 12 times with 8- to 10-ml portions of wash solution; larger amounts, such as 200 mg, should be washed at least 20 times.

Transfer the paper and precipitate to a weighed porcelain crucible large enough to hold the paper comfortably and dry at 45° C [9] for 4 to 5 hours or preferably overnight. Place in a cold muffle furnace and raise the temperature very gradually until smoking has ceased. Generally, about 2 or 3 hours are required. It is then safe to raise the temperature gradually to 1,000° C. Ignite for 30 minutes at this temperature, cool in a desiccator for 1 hour, and weigh as SnO_2. Ignite again to check for constant weight. Subtract the weight of the residue obtained in a blank carried through all the steps of the procedure. The weight of the blanks obtained in the experiments listed in tables 1 to 3 ranged from 0.1 to 0.3 mg and averaged 0.2 mg. The corrected weight of SnO_2 multiplied by 78.77 and divided by the weight of sample represents the percentage of tin.

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[5] This mixture consists of diluted hydrobromic acid (1+2) containing 5 ml of hydrochloric acid per 100 ml of solution. For 10 mg of tin use 30 ml of this mixture, for 50 mg use 60 ml, and for 200 mg use 140 ml.

[6] Cover the receiver with a filter paper having a center hole for the condenser outlet, and use this paper afterward for pulp by shaking it up with a little water.

[7] When dealing with materials of unknown tin content, it is advisable to test for completeness of distillation by distilling with an additional 25-ml portion of acid mixture, catching the distillate in a new receiver, and treating the second distillate with cupferron separately.

[8] The solution is diluted to the proper acidity rather than neutralized with ammonium hydroxide because ammonium bromide is apparently adsorbed by the precipitate, cannot be washed out completely, and causes loss of tin during ignition.

[9] This operation is conveniently done on top of a drying oven. Too rapid drying at higher temperatures will cause the precipitate to liquefy and spatter.

III. DISCUSSION OF PROCEDURE AND RESULTS

The separation of tin by distillation prior to precipitation appears to have definite advantages over other methods. Experiments on the precipitation of tin as the hydroxide, sulfide, and cupferron compound indicated that the last-named method was the most suitable for gravimetric work under the conditions following distillation. A number of interfering elements not removed by the McCay method are eliminated by distillation, as for example, iron, titanium, zirconium, gallium, and vanadium. In addition, distillation eliminates the danger of error caused by co-precipitation.

In the method described in this paper the distillation procedure of Scherrer [5] is modified and combined with the cupferron method for tin. As the volatile elements arsenic and antimony are frequently associated with tin, directions for the removal of arsenic and the bulk of the antimony are included. The removal of all the antimony is not sought as this requires considerable time, involves danger of loss of a small amount of tin by volatilization, and is, moreover, unnecessary as quinquevalent antimony in moderate amount (not over 20 mg) is not co-precipitated with tin by cupferron. Trivalent antimony is precipitated by cupferron.

In the absence of an excessive quantity of lead, it is possible to conduct the distillation without the preliminary separation of the tin as hydrated oxide. Lead in amounts sufficient to produce a heavy precipitate of lead sulfate causes bumping during distillation. More than 200 mg of lead cannot be handled in the apparatus.

Repeated trials have shown that approximately a sixfold excess of cupferron over stoichiometric requirements must be used to precipitate tin completely; a four-fold excess is insufficient. On the other hand, a too-generous excess must be avoided as the excess reagent precipitates in part and increases the danger of loss by spattering during the drying of the precipitate. This precipitate requires more than ordinary care in drying.

As stannic bromide is extremely volatile on ignition, particular care must be exercised in washing the paper and precipitate free from hydrobromic acid. Depending upon the size of the precipitate, 10 to 20 thorough washings on the filter paper with cold diluted cupferron solution (0.15 percent) are necessary. Large precipitates should be filtered and washed with the aid of moderate suction.

The results shown in table 1 indicate the accuracy that can be expected if tin is precipitated with cupferron under the conditions that would prevail after distillations as in the recommended procedure.

TABLE 1.—*Precipitation of tin with cupferron in diluted* HBr-HCl-H_2SO_4 *solution followed by ignition to* SnO_2

Tin		
Present	Found	Difference
g	*g*	*mg*
0.0750	0.0751	+0.1
.0750	.0752	+.2
.2011	.2009	−.2
.2023 [a]	.2025	+.2
.2098 [a]	.2099	+.1
.2583	.2582	−.1
.2587	.2588	+.1

[a] In these experiments, 0.0261 g and 0.0207 g of antimony, respectively, were added.

The results in table 2 indicate the accuracy that can be expected if the complete recommended procedure is applied to known amounts of tin.

TABLE 2.—*Results obtained by applying the recommended procedure to known amounts of tin*

Tin		
Present	Found	Difference
g	*g*	*mg*
0.0562	0.0562	±0.0
.0667	.0669	+.2
.1043	.1041	−.2
.1223	.1222	−.1
.2011[a]	.2014	+.3
.2021[a]	.2022	+.1
.2070	.2069	−.1
.2083	.2085	+.2
.2099	.2102	+.3
.2375	.2377	+.2

[a] In these experiments, 0.0178 g and 0.0280 g of antimony, respectively, were added.

The data in table 3 indicate the results obtained by applying the recommended procedure to copper-base and lead-base alloys.

TABLE 3.—*Determination of tin in copper-base and lead-base alloys*

Tin		Weight of sample	Material
Present	Found		
Percent	*Percent*	*g*	
0.96	0.966	5	Sheet brass, NBS Standard Sample 37c.[a]
	.966	5	
	.965	5	
.97	.973	5	Manganese bronze, NBS Standard Sample 62b.[b]
	.971	5	
	.968	5	
4.69	4.68	2	Ounce metal, NBS Standard Sample 124.[c]
	4.68	2	
7.83	7.81	1	Cast bronze, NBS Standard Sample 52a.[d]
	7.82	1	
9.76	9.77	1	Phosphor bronze, NBS Standard Sample 63a.[e]
	9.77	1	
5.06	5.05	1	Lead-base bearing metal, NBS Standard Sample 53b.[f]
	5.05	1	
	5.05	4	
	5.03	4	
34.88	34.88	0.5	Solder, NBS Standard Sample 127.[g]
	34.89	.5	
	34.90	.5	
	34.90	.6	
	34.90	.6	

Percentages of other constituents:
[a] 70 Cu; 27 Zn; 1 Pb; 0.2 Fe.
[b] 57 Cu; 38 Zn; 0.8 Fe; 0.3 Pb.
[c] 85 Cu; 5 Zn; 5 Pb.
[d] 88 Cu; 3 Zn; 0.05 Fe; 0.01 Pb.
[e] 78 Cu; 9 Pb; 0.6 Zn; 0.6 P; 0.5 Fe; 0.5 Sb; 0.03 As.
[f] 84 Pb; 10 Sb; 0.2 Cu; 0.04 As.
[g] 64 Pb; 0.8 Sb; 0.1 As; 0.01 Cu.

This method is applicable to other materials containing tin, such as aluminum alloys, zinc alloys, and steels following preliminary separations, as by the use of hydrogen sulfide when needed. It can be used for tin-base alloys containing 80 to 90 percent of tin and for tin ores, but in these cases, due to the limited amount of cupferron precipitate that can be conveniently handled, a small sample (0.2 to 0.3 g) must be taken, and the resulting accuracy is of the order of approximately 1 part in 800.

The number of elements that may interfere in the recommended procedure is small. Germanium, boron, and molybdenum may accompany tin on digestion with nitric acid, and may distill [10] in part, but of these only molybdenum, which is uncommon in nonferrous alloys, would be precipitated by cupferron. Scherrer [11] found that with 100 mg of molybdenum originally present, 0.3 mg was found with the tin after one distillation, and only 0.01 mg after a second distillation. It is thus apparent that danger of interference by molybdenum is slight, but should be kept in mind when working with materials containing this element.

IV. REFERENCES

[1] W. F. Hillebrand and G. E. F. Lundell, Applied Inorganic Analysis, p. 238 (J. Wiley & Sons, New York, N. Y., 1929).
[2] S. G. Clarke, Analyst **56**, 82 (1931).
[3] J. B. Ramsey and J. G. Blann, J. Am. Chem. Soc. **56**, 815 (1934).
[4] F. L. Okell and J. Lumsden, Analyst **60**, 803 (1935).
[5] J. A. Scherrer, J. Research NBS 21, **95** (1938) RP 1116.
[6] A. Kling and A. Lassieur, Compt. rend. **170**, 112 (1920).
[7] L. W. McCay, J. Am. Chem. Soc. **31**, 373 (1909).
[8] N. H. Furman, Ind. Eng. Chem. **15**, 1071 (1923).
[9] A. Pinkus and J. Claessens, Bul. soc. chim. Belg. **36**, 413 (1927).
[10] J. I. Hoffman and G. E. F. Lundell, J. Research NBS **22**, 465 (1939) RP 1198.
[11] J. A. Scherrer, J. Research NBS **16**, 253 (1936) RP871.

WASHINGTON, June 21, 1944.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1611

Part of Journal of Research of the National Bureau of Standards, Volume 33, October 1944

MACHINES AND METHODS FOR TESTING CORDAGE FIBERS

By Herbert F. Schiefer

ABSTRACT

Machines are described for testing the flexural endurance and the resistance to abrasion of cordage fibers. In the test for flexural endurance, a bundle of fibers having a twist of one turn per inch is repeatedly drawn back and forth over three small pulleys located at the vertices of an isosceles right triangle. In the test for resistance to abrasion, a similarly twisted bundle of fibers is drawn back and forth against a second bundle twisted once around the first. This test is made in such a way that the flexing of fibers during the test is reduced to a minimum.

The procedures for the selection of fibers, preparation of fiber bundles weighing 1 grains per 15 inches of length, and conditioning of test specimens are outlined. The unprocessed fibers were tested for the following: Fineness of fiber; dry and wet breaking strength and elongation; flexural endurance; resistance to abrasion; and the effect of elevated temperatures, continuous soaking in fresh and in salt water, alternate wetting and drying with fresh or salt water, and exposure to light with intermittent spraying with water. The results of tests of six lots of abaca, nine of sisal, two of jute, two of henequen, one of pita floja, one of ixtle, four of sansevieria, one of palmetto, three of hemp, two of roselle, one of manila, two of yucca, and one of malvita are given and discussed.

Great variations were found in the characteristics of different lots and grades of one kind of fiber. There was considerable overlapping in results of different kinds. No one kind of fiber was outstanding in all respects. Abaca was the strongest of the fibers tested, but some of the lots of abaca were weaker than some lots of sisal. Henequen and sisal were more resistant to abrasion than the other fibers tested, and they had higher flexural endurance, but were the least resistant to exposure to light and intermittent spraying with water. Pita floja, one of the strongest fibers tested, was one of the least resistant to abrasion. Sansevieria had exceptionally good strength. Hemp and jute were very similar in all of the characteristics measured. The resistance to abrasion of the fibers tested was profoundly affected by the direction of twist in the ply relative to that in the bundle, and also by the addition of a small amount of lubricant.

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I. INTRODUCTION

The development of machines and procedures for testing cordage fibers was undertaken by the National Bureau of Standards at the request of the Board of Economic Warfare, which acted on the advice of a committee from the War Production Board, and the United States Departments of Agriculture, War, Navy, and Commerce. The funds for the investigation were in part provided by the Defense Supplies Corporation. The proposed study was discussed with experts of the cordage industry. In addition to the development of machines and testing procedures, the study included the testing of standard grades of cordage fibers as well as proposed substitutes.

The purpose of this investigation was to provide means for the quick evaluation of the characteristics of experimentally grown fibers and of less known native fibers. A further purpose was to provide data on the characteristics of fibers long used in the manufacture of rope and cordage as a basis for judging the suitability of other fibers. These methods and data can be employed in the search for and in the quick development of sources of substitute fibers, and obviate the need for large quantities of fiber to be made into rope for determining the suitability of the fiber by testing the rope. The results of the study should also aid in the improvement of cordage fibers after the war, since means are provided for measuring the characteristics of fibers from a single leaf and for conducting systematic and carefully planned experiments.

The machines and methods developed are suitable for testing processed or unprocessed fibers for the following: Breaking strength and elongation when dry and when wet; flexural endurance; resistance to abrasion; fineness of fiber; and effect of elevated temperatures, continuous soaking in fresh or salt water, alternate wetting and drying with fresh or salt water, and exposure to light with intermittent spraying with fresh water. The machines and methods predescribed in this paper, and the results of tests on a number of fibers, are reported.

Bundles of fibers, weighing 5 grains per 15 in. of length (0.34 g/40 cm) and containing one turn of twist per inch of length were tested rather than individual fibers. This procedure was followed because the variation between individual fibers is so great as to make prohibitive the number of tests necessary for determining significant differences between kinds of fibers.

On the basis of the data presented, a number of fibers appear to be suitable as substitutes for abaca and sisal (hard) and jute (soft) fibers

as far as their mechanical characteristics are concerned. The production facilities and cost of these fibers were not considered. One outstanding result of this investigation was the profound effect that the direction of twist in the ply relative to that in the bundle had on the resistance to abrasion of the fibers, regardless of the kind of fiber tested. The amount of twist in the bundle and in the ply also affect the resistance to abrasion. A systematic study of the influence of the amount of twist would yield worth-while information and indicate the optimum twist to be used for each fiber in the manufacture of cordage and rope having a high resistance to abrasion.

II. TESTING PROCEDURES AND EQUIPMENT

1. SELECTION OF FIBERS AND PREPARATION OF FIBER BUNDLES

Wisps of fibers were drawn at random from different parts of the fiber lot to be tested. The wisps were stroked by hand to remove tangled masses of short fibers. They were inserted in a template, and sections 15 in. in length were cut from the wisps. These sections were taken at random along the length to provide sampling of the various parts of a fiber from base to tip. Enough fibers of a lot were cut at one time to provide an ample supply for all the tests. The cut fibers were placed randomly in parallel alinement in a box to make the sample distribution of fiber as uniform as practicable. Individual fibers were drawn at random from this box to make a bundle weighing 5 grains. Whenever practicable, the fibers in each bundle were counted and recorded. In preparing a bundle, care was taken to aline the ends as evenly as practicable. Fibers shorter than 15 in. and those of irregular type, such as split or fractured fibers, were discarded. The above procedure was followed in preparing bundles of the different kinds of fibers, except that for such fibers as jute, pita floja, and hemp, the number of fibers in the bundles were not counted. For these fibers it was too difficult to ascertain what constituted a fiber without the aid of some magnifying device, and counting the number of fibers in each bundle was impracticable.

2. FINENESS OF FIBER

From the large number of bundles prepared from each fiber lot, the average number of fibers per 5-grain 15-in. bundle was calculated as well as the standard error of this average. This number is related to the fineness of fiber by the equation $F=1750\,N$, where F is fineness of fiber in feet per pound, and N is the average number of fibers in a 5-grain 15-in. bundle.

For those fibers where it was impracticable to count the number in each bundle, a sample of the fibers 15 in. long was taken and weighed. The sample was then spread out in a fan-shaped pattern, and the number of fibers were counted with a widefield, low-magnification lens. A pair of sharp pick needles was found to be very helpful in separating the individual fibers while counting. Those fibers that separated very readily were considered as individual fibers, each fiber containing a group of elementary fiber cells. The number of fibers in a 5-grain 15-in. bundle was calculated from the number of fibers counted, usually more than 500, and from their weight and

length. The fineness of fiber was computed from the equati
$F=1750\ N$.

3. TWISTING DEVICE

The device for twisting the bundle of fibers is shown in figure
The bundle was fastened at one end in a clamp that can be rotat
with a crank. The other end was fastened in a clamp that is part of
compound pendulum pivoted at the bottom. The tension that th
pendulum exerts on the fibers can be adjusted by changing the positi
of a weight. A tension of 75 g was found to be satisfactory.
remains essentially constant throughout the twisting operation an
was used in the tests reported in this paper. The distance betwee
the two clamps is 10 in. at the beginning of the twisting operati
and slightly less at the end because of the lengthwise contraction
the bundle with twisting. The provision to permit contraction
essential in the twisting process. If it is lacking, the fibers may b
damaged because a high tension is produced owing to the inhere
low stretch of cordage fibers. A stop is provided to keep the pendulu
and clamp in a fixed relation to the rotatable clamp while insertin
the bundle.

4. BREAKING STRENGTH AND ELONGATION, DRY

The bundle of fibers was twisted one turn per inch of S-twist wi
the device described. The twisted bundle was removed from th
twisting device and placed across a board 12 in. wide fitted wi
slotted leather strips along the two sides to hold the bundle taut an
to prevent untwisting (fig. 2). In transferring the bundle, care wa
taken not to alter the twist. Two pairs of cardboard strips 1 i
wide and about one twenty-fifth inch thick were slipped under th
bundles at *A*, *B*, *C*, and *E* in figure 2. These strips were made paralle
to each other and were alined perpendicular to the length of th
bundles. The distances between cardboards from *A* to *B* and from
to *E* are 3 in. The bundles were glued to the cardboards with ca
penter's glue. The glue was allowed to dry and the fibers wer
conditioned for at least 12 hours in an atmosphere of 65-percen
relative humidity and 70° F. The bundles were cut in the middl
between cardboards *B* and *C*, thus forming two test specimens
each bundle. The cardboard strips were then nearly cut throug
between the bundles (fig. 3), leaving about 1-in. squares of cardboar
firmly attached to the ends of each half of the bundle of fibers.
specimen for test, readily detached from the remaining bundles b
tearing the cardboard, was inserted in the flat clamps of a pendu
lum-type machine of 110-lb capacity. The speed of the pullin
clamp was 12 ± 0.5 in./min.

The cardboards and glue protected the fibers from being damage
when clamped in the machine and effectively eliminated slippage
fibers in the clamps. The small cardboard strips also were an aid i
handling the bundles of fibers and in retaining the inserted twist

FIGURE 1.—*Device for twisting a bundle of fibers.*

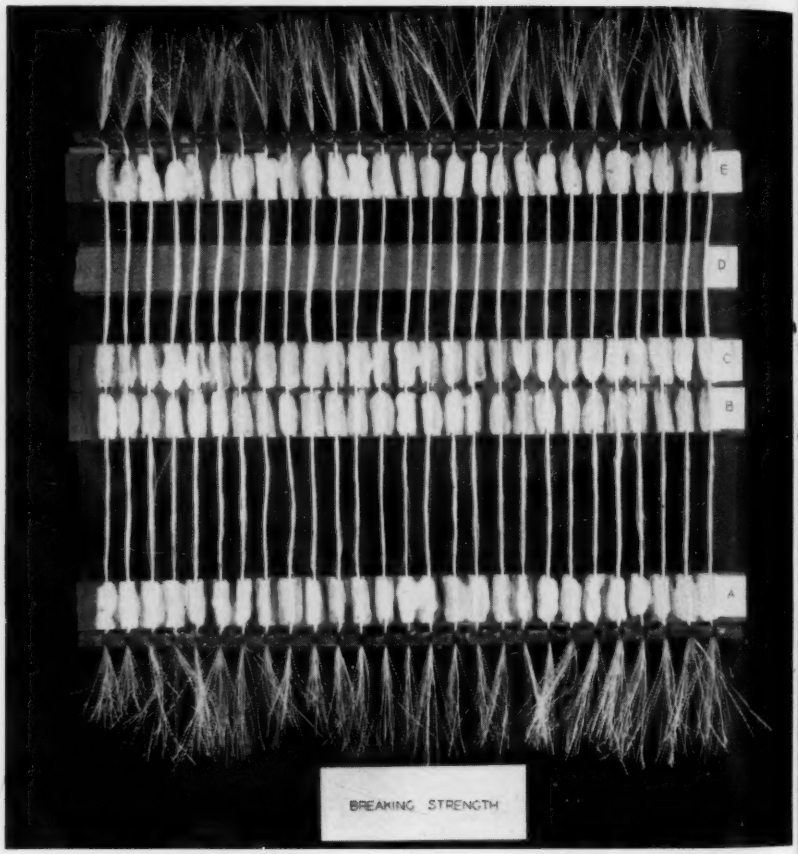

FIGURE 2.—*Board for holding twisted bundles of fibers during gluing to strips of cardboard.*

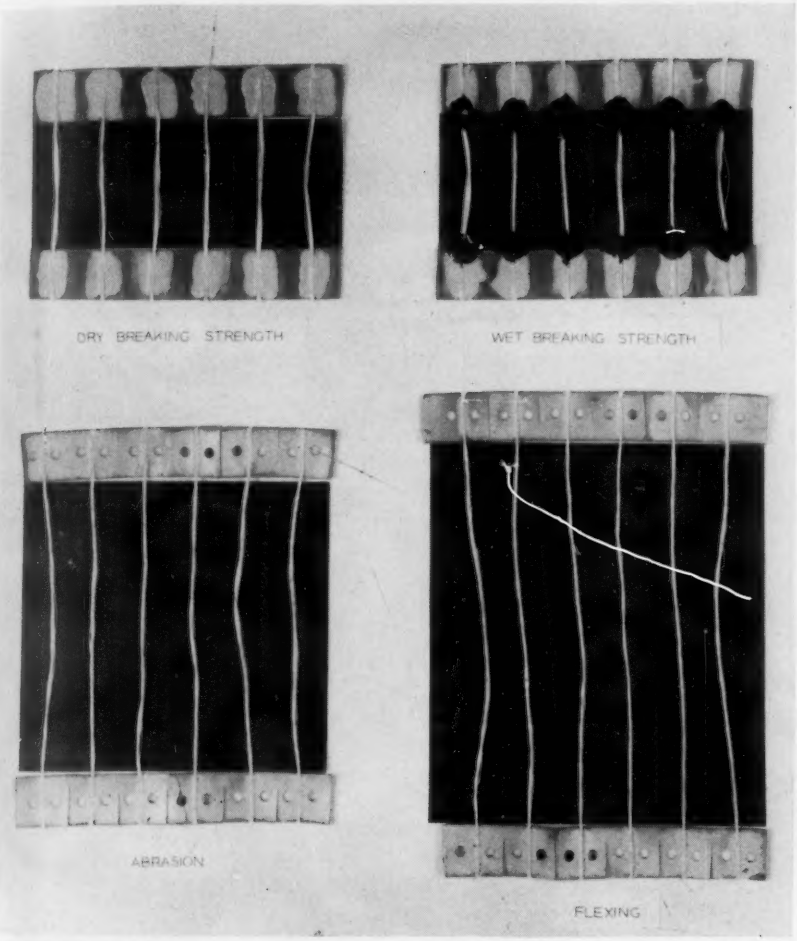

FIGURE 3.—*Twisted bundles of fibers glued to cardboards for tests of dry and wet breaking strength, resistance to abrasion, and flexural endurance.*

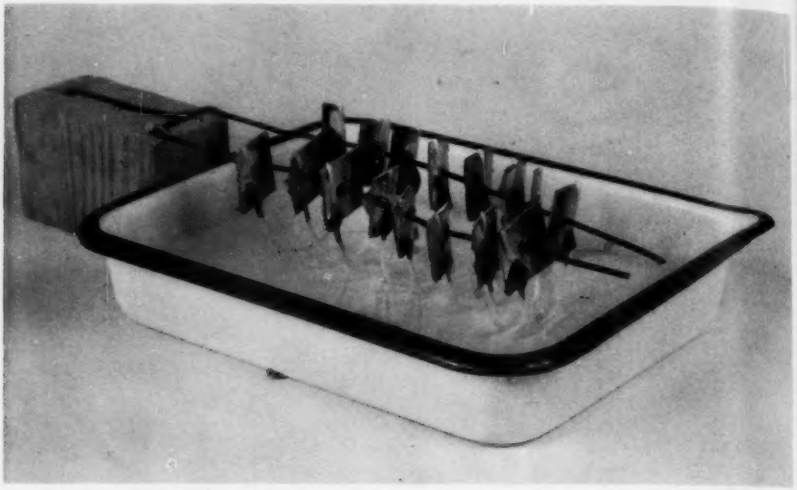

FIGURE 4.—*Bundles of fibers partially immersed in water for tests of wet strength.*

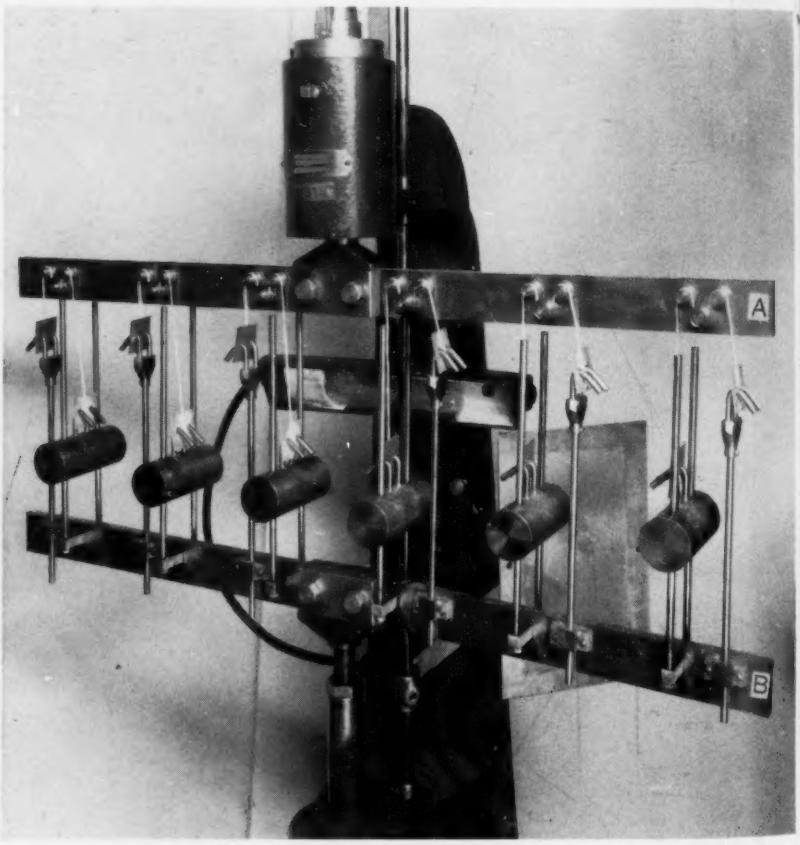

FIGURE 5.—*Machine for testing the flexural endurance of bundles of fibers.*

The breaking strength and elongation were read from the scale and load-elongation curve. Fifty or more tests were usually made of each fiber lot. The average strength and elongation were calculated, as well as their standard errors. The breaking length of the bundle, that is, the length which would be just sufficient to break it under its own weight, was computed from the breaking strength and bundle weight and length, and is given by $L=1750\ B$, where L is breaking length in feet and B is breaking strength in pounds.

5. BREAKING STRENGTH AND ELONGATION, WET

The bundles of fibers for tests of the wet strength were twisted, mounted on boards, and glued to strips of cardboard in the same manner as for tests of the dry strength. After the glue was dry a drop of hot ceresin was applied at the juncture of the fibers and the cardboard. This wax was applied with a hot copper tubing bent into the shape of a large pen. The wax is shown by a black discoloration of the bundles labeled "wet breaking strength" in figure 3. It effectively prevented the water from coming in contact with the cardboard and glue during soaking of the fibers. The bundles were cut in the middle as for tests of the dry strength, thereby forming two test specimens of each bundle. A hole, not shown in figure 3, was then punched in the cardboard at each end of the specimen. The cardboard was cut between the bundles as for the dry strength tests. Each bundle was then detached, formed into a U-shaped specimen, and strung on two long horizontal prongs through the punched holes (fig. 4). Care was taken to preserve the twist. The bundles were spaced far enough apart to avoid contact between them. This separation was essential to prevent water from rising between the fibers to the glue and cardboard. The bundles were placed over a flat dish containing water (fig. 4). The bottom of the U-shaped specimen was submerged about 1 in. into the water and allowed to soak overnight. One bundle at a time was then removed and immediately tested for wet breaking strength and elongation in the same manner as the dry bundles. The water that dripped from the fibers to the glued cardboard, which was fastened in the lower clamp, was in contact for such a short time that the cardboard and glue were not affected. The same number of tests and calculations were made as for the dry strength tests.

6. FLEXURAL ENDURANCE

The bundles of fibers for the flexural endurance tests were twisted one turn per inch of S-twist and then mounted on boards the same as for tests of the dry strength, except that they were spaced twice as far apart. They were glued to two strips of cardboard, the free length between the cardboards was 8 in. After the glue was dry, two holes were punched in the cardboard at the ends of each bundle, as illustrated in figure 3 for those labeled "flexing." The cardboard was cut between the bundles as was done in tests for strength. A bundle was then detached and tested with the machine shown in figure 5.

Six twisted bundles of fibers are drawn back and forth simultaneously over three small pulleys 5/16 in. in diameter located at the vertices of an isosceles right triangle, the hypotenuse being 7/8 in. The ball-bearing pulleys are attached to a fixed horizontal bar, *A*. A second horizontal bar, *B*, is attached to the shaft of a reciprocating mechanism, not shown, having a total stroke of 4 in. For each specimen the reciprocating bar contains a fixed rod with two prongs, to which the punched cardboard, glued to one end of the bundle of fibers, is attached. It also contains a pair of parallel rods which serve to guide the free up-and-down movement of a 1-lb weight. The weight contains two prongs, to which the punched cardboard glued to the other end of the bundle is attached. The twisted fibers are passed over the three pulleys as indicated in figure 5. The twist is retained by the manner of attachment described, and tension is exerted by the weight during the back-and-forth movement of the fibers over the pulleys. A complete back-and-forth movement is called a flexing cycle. The machine operates at 60 cycles per minute. The number of cycles is recorded by a counter, which is not shown in the figure.

The six bundles of fibers mounted in the machine at a time were flexed for a preassigned number of cycles, after which their breaking strengths were determined. This procedure was repeated until a sufficient number had been tested to give a well-determined curve relating the breaking strength and number of flexing cycles. The number of cycles required to reduce the breaking strength to 50 percent of the dry breaking strength and to a breaking strength of 20 lb were recorded from this curve.

7. RESISTANCE TO ABRASION

The bundles of fibers for the tests of the resistance to abrasion were twisted one turn per inch of S-twist and mounted on boards the same as for tests of the dry strength except that they were spaced twice as far apart. They were glued to two strips of cardboard, at *A* and *D* only (fig. 2). The free length between *A* and *D* was 6 in. After the glue was dry, two holes were punched in the cardboard at the ends of each bundle, as illustrated in figure 3 for those labeled "abrasion." The cardboard was cut between the bundles in the same manner as for tests for strength. The bundles were then detached and tested for resistance to abrasion with the machine shown in figure 6. In this test a twisted bundle of fibers is drawn back and forth longitudinally against a second bundle that is twisted once around the first. Six pairs of bundles are tested simultaneously.

A motor speed reduction unit with a double-acting crankshaft imparts a reciprocating motion to two rods which move exactly out of phase. To each rod is attached a horizontal bar containing six pairs of prongs. The punched cardboard, glued to one end of a twisted bundle, is attached to a pair of prongs of one bar. The punched cardboard, glued to the other end of the bundle, is attached similarly to two prongs of a plate located directly below, and which is constrained to move in a guide inclined 4½ degrees to the vertical.

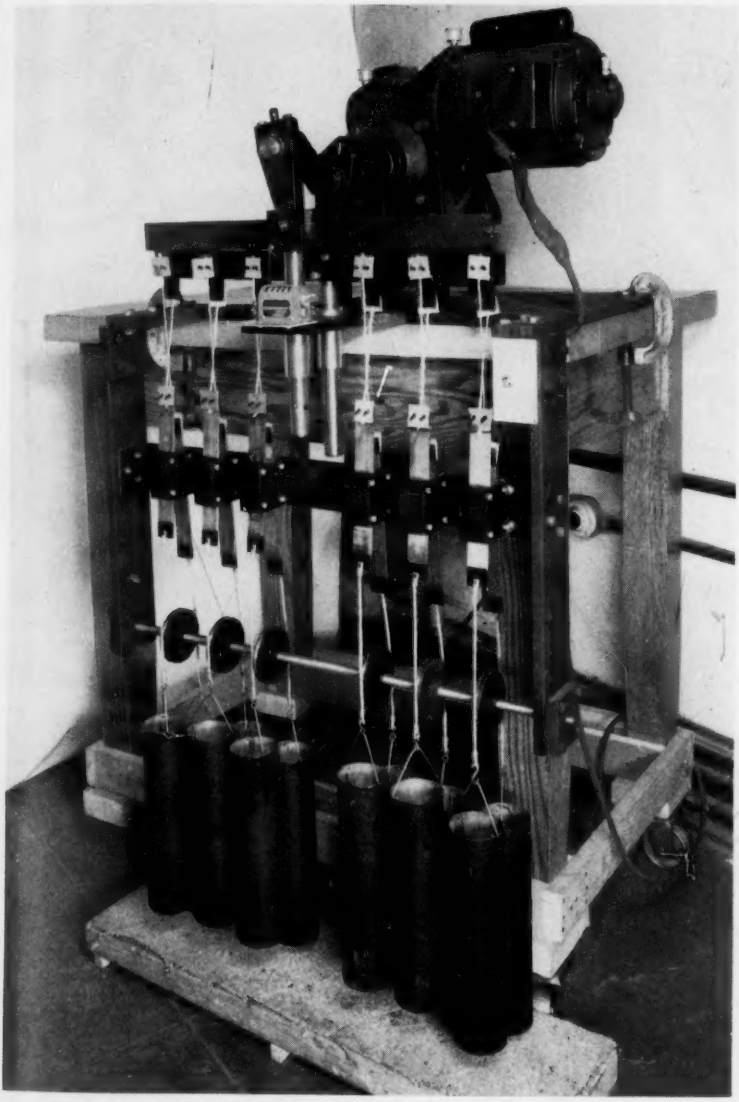

FIGURE 6.—*Machine for testing the resistance to abrasion of bundles of fibers.*

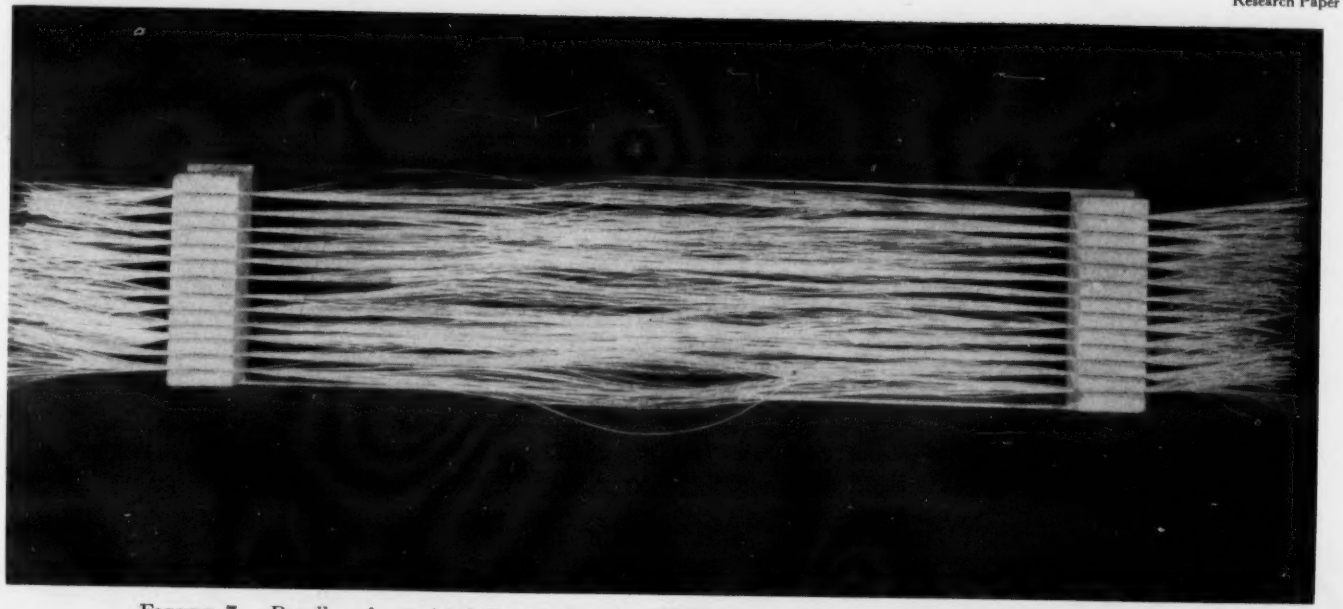

FIGURE 7.—*Bundles of untwisted fibers mounted on a board for accelerated weathering in Weather-ometer.*

Similarly, the second bundle of a pair is attached to the second bar at the top and to a second plate at the bottom. The latter is also constrained to move in a guide inclined 4½ degrees to the vertical. The inclination of the two guide plates is toward each other, with an internal angle equal to 9 degrees. The S-twist of each bundle is preserved when mounting the bundles and while twisting the second bundle of each pair one turn of S-twist around the first.

A can containing lead shot is attached to the lower end of each plate by means of a metal cable. The motions of the metal cables are guided by ball-bearing idler pulleys to prevent the cans from touching each other. The total weight of each can is adjustable. A weight of 5 lb was found to be satisfactory and was used for the fibers tested. The two bundles of a pair intersect with an angle of about 9 degrees, and this angle, as well as the twist, is essentially maintained during each complete back-and-forth movement, or cycle, of abrasion. The machine operates at 60 cycles per minute. The number of cycles is recorded by a counter located directly in front of the rods.

The six pairs of bundles tested at a time in the machine were abraded for a preassigned number of cycles, after which their breaking strengths were determined. This procedure was repeated until a sufficient number had been tested to give a well-determined curve relating the breaking strength and the number of cycles of abrasion. The number of cycles required to reduce the breaking strength to 50 percent of the dry breaking strength and to a breaking strength of 20 lb were recorded from this curve.

The above procedure was repeated, except that the second bundle of each pair was twisted one turn of Z-twist around the first. A few tests were also made according to the above procedure but with a drop of lubricating oil added to each pair of bundles.

8. ACCELERATED WEATHERING

The accelerated weathering tests were made by exposing bundles of untwisted fibers to light, using the type DL–TS Weather-ometer. The essential features of this unit are two glass-enclosed carbon arcs, each arc operating on 110-volt 60-cycle alternating current. The arc current is between 15 and 17 amperes. In each arc two carbons are used at the bottom and one at the top. Either a No. 20 cored carbon was used at the top and two No. 70 solid carbons were used at the bottom, or a No. 70 solid carbon was used at the top and two No. 20 cored carbons were used at the bottom. The samples were mounted on the inside of a cylindrical drum, which rotates around the arcs at 1 rpm. Thirty samples were exposed at a time. Each sample contains 12 bundles of fibers mounted on a special board, as shown in figure 7.

A vertical bank of four nozzles is provided for spraying the fibers with water. They rotate past this bank once each minute. The water spray is automatically turned on for a 3-minute period once every 20 minutes. A thermostat is provided to prevent the maximum temperature at the fibers from exceeding 140° F. No provision is made for controlling the minimum temperature except by the water spray and temperature of the water. Provision is made for cooling the drum by a spray on the outside of the drum. A timing device records the number of hours of operation.

The bundles of fibers were exposed continuously to light and to intermittent spraying with water. At the end of a preassigned number of hours of exposure, a board containing 12 bundles of fibers was removed for each lot of fiber for tests of their strength. The exposure of the remaining boards of fibers was continued. They were likewise withdrawn for tests of their strength at the end of a preassigned number of hours of exposure.

The 12 bundles of exposed fibers from each board were removed, one at a time, twisted one turn per inch of S-twist, and mounted on a board and glued to four strips of cardboard in the same manner as for tests of dry strength, and two tests were made of each bundle. The average strength and standard error were calculated from the test results obtained for each exposure time of a fiber lot.

9. RESISTANCE TO ELEVATED TEMPERATURE

Thirty-six bundles of untwisted fibers from each lot of fiber to be tested were placed in an electric oven maintained at 105° to 110° C (221° to 230° F). The air in the oven was circulated by a fan. Twelve bundles of fibers from each lot of fiber were removed from the oven at the end of 10, 20, and 30 days exposure. The exposed fibers were then twisted one turn per inch of S-twist and mounted for tests of strength in the same manner as for dry strength, and two tests were made of each bundle. The average strength and standard error were calculated from the 24 test results obtained for each exposure time of a fiber lot.

10. RESISTANCE TO CONTINUOUS WETTING WITH FRESH OR SALT WATER

Fifty bundles of untwisted fibers from each lot of fiber to be tested were placed in a beaker containing tap water. The water was renewed each day. One half of the bundles were soaked for 12 days and the other half for 28 days.

The soaked fibers were allowed to dry, after which they were twisted ne turn per inch of S-twist, and mounted on boards for tests of trength in the same manner as for dry strength. Two tests were ade of each bundle. The average strength and standard error and verage elongation and standard error were calculated from the 50 est results obtained for each soaking time of a fiber lot.

The above procedure was repeated but water containing 3.7 percent f sea salt was used instead of tap water. The salt water was renewed ach day.

11. RESISTANCE TO ALTERNATE WETTING AND DRYING WITH FRESH OR SALT WATER

Twenty-five bundles of untwisted fibers from each lot of fiber to be ested were placed in a beaker containing tap water. The bundles ere removed after 24 hours of soaking and allowed to dry for 24 hours. he wetting and drying cycle was repeated 12 times; a new supply of ater was used for each cycle. At the end of the twelfth cycle each undle was twisted one turn per inch of S-twist, and then mounted on oards for tests of strength in the same manner as for dry strength. wo tests were made of each bundle. The average strength and standrd error and average elongation and standard error were calculated rom the 50 test results of each fiber lot.

The above procedure was repeated but water containing 3.7 percent f sea salt was used instead of tap water. The salt water was renewed r each wetting and drying cycle.

III. MATERIALS TESTED

The fibers tested included six lots of abaca (manila), nine of sisal, wo of jute, two of henequen, one of pita floja, one of ixtle, four of ansevieria, one of palmetto, three of hemp, two of roselle, one of anzanita, one of malvita, and two of yucca. The number assigned o each fiber and information as to grade, source, housemark, and ate of baling, which are considered important in the cordage industry, re given in table 1.

TABLE 1.—*Description, fineness, and breaking strength of cordage fibers*

[The standard error* is given immediately after each value in the table]

Number	Fiber	Description and grade	Number of fibers per 15-in. bundle weighing 5 grains	Fineness of fiber	Breaking length of dry bundle	Breaking strength of bundle		Dry breaking strength after—			
								Soaking in fresh water for—		Soaking in salt water for—	
						Dry	Wet	12 days	28 days	12 days	28 days
				1,000 ft /lb	*1,000 ft*	*lb*	*lb*	*lb*	*lb*	*lb*	*lb*
1	Abaca	Grade E, Davao, Housemark TO/KSO/E. Baling date Dec. 1939.	30 ±0.9	53 ±1.6	158 ±4.2	90 ±2.4	74 ±1.8	68 ±2.4	49 ±1.6	93 ±2.0	83 ±2.3
2	do	Grade J2, Davao, Housemark DA/KC/J2. Baling date Sept. 1941.	30 ±0.7	53 ±1.2	180 ±2.3	103 ±1.3	96 ±1.9	73 ±2.7	28 ±2.0	51 ±1.4	58 ±1.7
3	do	P. I. Govt., Grade I	28 ±0.5	49 ±0.9	*166 ±5.4	*95 ±3.1	*62 ±4.3	84 ±1.5	88 ±1.9	85 ±1.9	72 ±1.7
4	do	P. I. Govt., Grade E, S F Co. Inc. Sta. Ana, Davao 55-19C Mindanao, Nov. 17, 1936, Da/SFC/E.	55 ±1.1	96 ±1.9	*142 ±4.0	*81 ±2.3	*57 ±2.6	68 ±2.1	61 ±2.0	67 ±1.6	67 ±1.3
5	do	P. I. Govt., Grade F, Saleeby Fiber Co., Manila 6-220 S. Can, Jan. 10, 1936, M/Sec/F.	52 ±2.5	91 ±4.4	*138 ±4.2	*79 ±2.4	*66 ±2.9	87 ±3.3	83 ±3.0	85 ±2.4	78 ±1.7
6	do	P. I. Govt., Grade J1, Fobuana Plant Co., Inc., Daliaom Davao, 57-136 S Min. Feb. 7, 1936, DL/FPC/J1, Sup. Seconds.	46 ±0.9	81 ±1.6	*133 ±4.2	*76 ±2.4	*59 ±2.8	82 ±1.5	77 ±2.0	83 ±1.8	70 ±1.4
7	Sisal	Grade 1, Housemark HIMO. Baling date Aug. 1942.	21 ±0.2	37 ±0.4	119 ±2.6	68 ±1.5	62 ±1.8	63 ±1.3	68 ±1.3	72 ±1.5	75 ±1.3
8	do	Grade 1	23 ±0.2	40 ±0.4	119 ±3.0	68 ±1.7	63 ±1.4	63 ±1.3	61 ±1.2	72 ±1.4	74 ±1.7
9	do	Grade 3L, Housemark LUCY. Baling date Aug. 1942.	19 ±0.2	33 ±0.4	126 ±2.5	72 ±1.4	56 ±1.2	56 ±1.1	58 ±1.1	75 ±1.6	79 ±2.3
10	do	Grade 3L	24 ±0.3	42 ±0.5	149 ±2.3	85 ±1.3	69 ±0.9	69 ±1.5	64 ±1.1	73 ±1.6	73 ±1.8
11	do	African, Grade 8	32 ±0.6	56 ±1.1	117 ±2.5	67 ±1.4	60 ±1.6	60 ±1.3	64 ±1.3	64 ±1.5	57 ±1.4
12	do	African, Grade 3L	30 ±0.4	53 ±0.7	100 ±1.4	57 ±0.8	59 ±1.4	68 ±1.1	65 ±1.4	61 ±1.0	61 ±1.2
13	do	African, Grade 8LT3	27 ±0.5	47 ±0.9	116 ±2.1	66 ±1.2	51 ±1.3	62 ±1.2	62 ±1.2	61 ±1.0	65 ±1.0
14	do	African, Grade LLT-A	37 ±0.7	65 ±1.2	135 ±2.5	77 ±1.4	65 ±2.0	64 ±1.0	72 ±1.3	63 ±1.2	65 ±1.1
15	do	Blend of several grades	21 ±0.2	37 ±0.4	100 ±2.8	57 ±1.6	55 ±0.7	57 ±0.9	56 ±0.8	61 ±1.0	56 ±0.9
16	Henequen	Grade C & M	20 ±0.1	35 ±0.2	86 ±1.4	49 ±0.8	41 ±0.9	46 ±0.9	47 ±0.7	54 ±0.9	52 ±0.8
17	do	Mexican, Grade A	21 ±0.2	37 ±0.4	86 ±1.4	49 ±0.8	43 ±0.5	48 ±1.0	49 ±0.8	50 ±0.8	51 ±0.8
18	Pita floja		**142 ±4.2	**249 ±7.4	152 ±2.3	87 ±1.3	61 ±1.2	55 ±1.5	53 ±2.1	80 ±1.9	76 ±2.2
19	Jute	High grade	**500 ±17	**880 ±30	93 ±2.3	53 ±1.3	44 ±1.2	45 ±1.3	40 ±1.0	54 ±1.5	53 ±1.5
20	do	Low grade	**280 ±55	**490 ±96	75 ±2.3	43 ±1.3	36 ±1.1	40 ±1.0	37 ±1.5	38 ±1.1	41 ±1.2
21	Hemp	Wis., Line No. 1	**160 ±18	**280 ±32	130 ±3.0	74 ±1.7	42 ±1.3	44 ±1.1	31 ±1.1	59 ±1.8	45 ±1.3
22	do	Wis., Line No. 3	**100 ±7	**175 ±12	70 ±1.9	40 ±1.1	24 ±0.8	29 ±1.0	22 ±0.8	33 ±1.2	25 ±0.8
23	do	Kentucky	**94 ±3	**135 ±5	58 ±2.6	33 ±1.5	19 ±0.9	22 ±0.8	26 ±1.0	27 ±1.3	31 ±1.1

26	Manzanita	Malvaviscus Arboreus	**105 ±12	**340 ±21	56 ±2.3	32 ±1.3	30 ±0.9	28 ±0.9	33 ±1.1	23 ±1.3	28 ±1.4
26	Malvita	Urena Lobata L.	**310 ±30	**540 ±53	53 ±2.3	30 ±1.3	35 ±1.3	34 ±1.1	28 ±1.0	32 ±1.3	30 ±1.3
27	Roselle	Hebiscus sabdariffa	**164 ±8	**287 ±14	81 ±2.1	46 ±1.2	47 ±1.6	44 ±1.4	44 ±1.6	42 ±1.6	45 ±1.9
28	Sansevieria	Metallica, Floridan	*120 ±2.8	*210 ±4.9	144 ±3.3	82 ±1.9					
29	do	Metallica, Floridan	*107 ±3.0	*187 ±5.3	120 ±3.0	74 ±1.7					
30	do	Guineensis, Floridan	**79 ±4.2	**138 ±7.4	152 ±4.4	87 ±2.5					
31	do	African	*94 ±2.3	*165 ±4.0	137 ±2.8	78 ±1.6					
32	Yucca elata	Bear grass	**97 ±5.2	**170 ±9.1	*61 ±2.8	*35 ±1.6					
33	Yucca macrocarpa.	Spanish bayonet	**30 ±1.3	**53 ±2.3	**128 ±4.0	**73 ±2.3					
34	Irtle	Maguey, Mexican	**21 ±0.7	**37 ±1.2	*74 ±2.1	*42 ±1.2					
35	Palmetto		*16 ±1.0	*28 ±1.8	**37 ±3.5	**21 ±2.0	**24 ±2.2				

* The standard error was computed by means of the expression $\sqrt{\frac{\Sigma d^2}{n(n-1)}}$, where d represents the deviations of the observed values from the average and n represents the number of observed values. Two asterisks indicate that n was 10 or more, one asterisk indicates that n was 20 or more, and no asterisk indicates that n was 50 or more.

TABLE 1.—*Description, fineness, and breaking strength of cordage fibers*—Continued

Number	Fiber	Description and grade	Dry breaking strength after—							
			12 cycles of soaking and drying in—		Heating to 105° C for—			Exposure in twin arc Weather-ometer for—		
			fresh water	salt water	10 days	20 days	30 days	100 hours	150 hours	200 hours
			lb	lb	lb	lb	lb	lb	lb	lb
1	Abaca	Grade E, Davao, Housemark TO/KS/O/E. Baling date Dec. 1939.	81 ±1.5	88 ±1.8	*85 ±1.8	*72 ±2.6	*52 ±2.6	*60 ±1.3		[b] 48 ±1.0
2	do	Grade J2, Davao, Housemark DA/KC/J2. Baling date Sept. 1941.	74 ±2.5	54 ±1.8	*75 ±1.6	*54 ±1.5	*48 ±1.5	*59 ±2.0	*51 ±1.2	*44 ±1.9
3	do	P. I. Govt., Grade I	76 ±2.2	76 ±2.4	*74 ±2.0	*67 ±1.8	*60 ±2.0	*52 ±3.7	*49 ±3.7	*18 ±2.4
4	do	P. I. Govt., Grade E, S F Co. Inc., Sta. Ana, Davao 55-19C Mindanao, Nov. 17, 1936, Da/SFC/E.	62 ±2.7	64 ±1.4	*70 ±2.9	*58 ±3.1	*47 ±2.2	*33 ±2.5	*31 ±2.6	*37 ±3.3
5	do	P. I. Govt., Grade F, Saleeby Fiber Co., Manila 6-220 S. Can. Jan. 10, 1936, M/Sec/F.	82 ±3.8	85 ±2.5	*68. ±2.1	*56 ±2.0	45 ±2.8	*40 ±2.9	*42 ±3.0	*31 ±2.5
6	do	P. I. Govt., Grade J1, Fobuana Plant Co., Inc. Daliaom Davao, 57-136 S Min. Feb. 7, 1936, DL/FPC/J1, Sup. Seconds.	80 ±1.7	72 ±2.1	*74 ±1.6	*72 ±1.4	*69 ±2.0	*43 ±3.2	*49 ±4.2	*45 ±2.0
7	Sisal	Grade 1, Housemark HIMO. Baling date Aug. 1942.	63 ±1.4	72 ±1.3	*62 ±1.4	*56 ±1.3	*51 ±1.3	*51 ±2.2		[b] 0
8	do	Grade 1	70 ±1.3	60 ±1.3	*59 ±1.1	*51 ±1.5	*44 ±1.2	*39 ±2.6		[b] 0
9	do	Grade 3L, Housemark LUCY. Baling date Aug. 1942.	58 ±1.3	68 ±1.2	*67 ±1.4	*62 ±1.5	*57 ±1.4	*57 ±1.6	*48 ±2.8	0
10	do	Grade 3L	73 ±1.2	73 ±1.2	*67 ±1.6	*61 ±1.5	*55 ±1.3	*55 ±1.1		[b] 0
11	do	African, Grade 8	63 ±1.5	55 ±1.1	*63 ±1.7	*59 ±0.9	*55 ±1.9	*49 ±2.1	*34 ±3.4	*19 ±3.9
12	do	African, Grade 3L	60 ±1.1	58 ±1.0	*30 ±1.6	*13 ±1.5	*4 ±0.9	*53 ±2.0	*39 ±2.8	*4 ±2.2
13	do	African, Grade 8LT3	68 ±0.9	57 ±1.4	*59 ±1.5	*52 ±1.1	*46 ±1.2	*58 ±2.8	*46 ±2.5	*6 ±3.2
14	do	African, Grade LLT-A	66 ±1.1	65 ±1.2	*69 ±1.5	*59 ±1.7	*50 ±1.2	*58 ±1.3	*50 ±1.9	*16 ±3.3
15	do	Blend of several grades	55 ±0.9	54 ±0.9	*53 ±0.9	*50 ±1.2	*46 ±1.6	*35 ±1.5	*22 ±1.7	0
16	Henequen	Grade C & M	53 ±1.0	53 ±0.8	*52 ±1.4	*52 ±1.5	*52 ±2.0	*30 ±1.5		[b] 1 ±0.5
17	do	Mexican, Grade A	53 ±0.7	49 ±0.7	*41 ±1.0	*36 ±1.0	*32 ±0.5	*35 ±1.5		[b] 0
18	Pita flojs		81 ±1.4	87 ±2.0	*72 ±2.2	*63 ±2.4	*58 ±2.3	*60 ±2.4		[b] 49 ±1.5
19	Jute	High grade	47 ±1.4	51 ±1.4	*40 ±1.6	*36 ±1.6	*32 ±1.1	*41 ±1.6		[b] 15 ±2.6
20	do	Low grade	41 ±1.2	39 ±1.7	*36 ±1.0	*30 ±1.0	*23 ±1.1	*29 ±2.0		[b] 0
21	Hemp	Wis., Line No. 1	45 ±1.6	49 ±1.4	*47 ±2.2	*37 ±2.4	*34 ±2.4	*50 ±2.2	*46 ±2.1	*35 ±1.1
22	do	Wis., Line No. 3	28 ±1.1	33 ±1.0	*32 ±1.5	*24 ±1.6	*16 ±1.5	*29 ±1.0	*29 ±1.4	*24± 1.2
23	do	Kentucky	27 ±1.0	31 ±1.1	*29 ±1.9	*23 ±1.3	*18 ±1.8	*35 ±2.9	*31 ±1.8	*27 ±1.4
24	Roselle	Hibiscus cannabinus (kenaf)	35 ±1.1	39 ±1.1	*40 ±1.7	*35 ±2.0	*30 ±1.8	*42 ±2.4	*27 ±2.1	*18 ±2.0
25	Manzanita	Malvaviscus Arboreus	31 ±1.3	29 ±1.3	*31 ±1.9	*27 ±1.6	*28 ±1.4	*26 ±2.6	*13 ±2.1	*8 ±2.3
26	Malvita	Urena Lobata L	30 ±1.0	32 ±1.3	*37 ±2.1	*39 ±1.7	*32 ±2.0	*23 ±2.5	*7 ±1.8	*5 ±1.0

24	Bromelia	Ochroma concolor (Kozak)	35 ±1.1	39 ±1.1	*40 ±1.7	*38 ±2.0	*30 ±1.5	*42 ±2.4	*37 ±2.1	*38 ±2.3	
25	Manzanita	Malvaviscus Arboreus	31 ±1.3	29 ±1.3	*31 ±1.9	*27 ±1.6	*28 ±1.4	*26 ±2.6	*19 ±2.1	*8 ±2.0	
26	Malvita	Urena Lobata L.	30 ±1.0	33 ±1.3	*37 ±2.1	*30 ±1.7	*32 ±2.0	*23 ±2.5	*17 ±1.6	*5 ±1.6	
27	Roselle	Hibiscus Sabdariffa	32 ±1.2	33 ±1.3	*37 ±2.1	*30 ±1.7	*32 ±2.0	*23 ±2.5	*17 ±1.6	0	
28	Sansevieria	Metallica, Floridan	40 ±1.6	38 ±1.8	*47 ±2.2	*50 ±1.5	*38 ±2.0	*33 ±2.3	*21 ±2.1		
29	do	Metallica, Floridan									
30	do	Guineensis, Floridan									
31	do	African									
32	Yucca elata	Bear grass									
33	Yucca macrocarpa.	Spanish bayonet									
34	Ixtle	Maguey, Mexican									
35	Palmetto										

* The value is for an exposure of 183 hours in Weather-ometer.

IV. RESULTS

In table 1 are also given the following data: Number of fibers pe bundle; fineness of fiber; breaking length; dry and wet breakin strength; and dry breaking strengths after (a) soaking in fresh and i salt water, (b) alternate wetting and drying with fresh and with sal water, (c) exposure to a temperature of 105° C, and (d) exposure to ligh and intermittent spraying with water in a Weather-ometer. The stand ard error is also given for each value reported in the table. All th values are based on bundles of fibers weighing 5 grains and 15 in. long.

In table 2 are given the following data: Dry and wet elongation a rupture; dry elongation at rupture after soaking in fresh and in sal water; and dry elongation after alternate wetting and drying by th use of fresh or salt water. The flexural endurance, the resistance t abrasion for S-twist in the bundles of fibers and S-twist in the ply o two bundles, and the resistance to abrasion for S-twist in the bundle of fibers, and Z-twist in the ply of two bundles are also given in table 2 The standard error is given for the dry and wet elongation values.

Number	Fiber	Elongation at rupture		Dry elongation at rupture after—						Flexural endurance at—		Resistance to abrasion for—			
				Soaking in fresh water for—		Soaking in salt water for—		12 cycles of soaking and drying in—				SS [a] twist at—		SZ [b] twist at—	
		Dry	Wet	12 days	28 days	12 days	28 days	Fresh water	Salt water	50% of original strength	Strength of 20 lb	50% of original strength	Strength of 20 lb	50% of original strength	Strength of 20 lb
		%	%	%	%	%	%	%	%	*Cycles*	*Cycles*	*Cycles*	*Cycles*	*Cycles*	*Cycles*
1	Abaca	[c] 2.1 ± 0.06	[c] 2.4 ± 0.17	2.8	2.1	2.3	2.8	2.5	3.2	475	950	900	1,400	1,400	2,200
2	do	2.8 ± 0.11	4.0 ± 0.12	3.4	2.1	2.6	3.1	3.5	2.2	215	550	800	1,250	1,800	2,900
3	do	[c] 3.9 ± 0.25		3.2	3.1	3.6	2.9	3.0	2.9	300	750	770	1,220	1,350	2,100
4	do	[c] 1.9 ± 0.15		2.7	2.0	2.4	2.3	2.6	2.8	300	525	750	1,120	3,400	5,000
5	do	[c] 2.8 ± 0.19		2.7	2.9	3.2	3.0	3.3	3.0	900	1,350	1,280	1,900	4,900	7,500
6	do	[c] 3.3 ± 0.19		3.1	3.1	3.4	2.9	3.4	3.3	750	1,150	2,930	4,300	6,400	12,000
7	Sisal	2.6 ± 0.08	2.9 ± 0.11	2.3	2.7	2.8	3.4	2.5	2.7	550	1,100	1,050	1,500	4,500	6,200
8	do	2.7 ± 0.07	4.0 ± 0.14	3.1	3.1	4.3	3.8	2.5	3.6	500	950	2,300	3,300	11,000	16,000
9	do	2.5 ± 0.04	3.0 ± 0.09	2.8	2.4	2.6	2.6	2.5	2.8	425	900	600	900	6,000	8,500
10	do	3.0 ± 0.06	2.7 ± 0.07	2.8	2.3	3.3	3.6	3.3	3.0	550	1,600	750	1,150	5,000	7,800
11	do	3.3 ± 0.08	3.8 ± 0.12	3.8	3.2	4.0	2.8	3.5	3.6	875	1,550	1,450	2,150	20,000	29,000
12	do	2.6 ± 0.07	2.6 ± 0.08	3.2	3.0	3.0	3.2	3.2	2.8	650	1,150	1,300	1,700	3,000	3,800
13	do	3.3 ± 0.10	4.4 ± 0.11	3.2	3.5	3.3	3.6	3.5	2.8	425	1,200	1,250	1,700	22,000	30,500
14	do	3.4 ± 0.10	3.6 ± 0.09	3.5	3.1	3.2	3.1	3.5	3.6	600	1,200	1,350	1,650	5,600	8,200
15	do	2.9 ± 0.10		3.2	3.0	3.6	2.6	3.2	2.6	550	950	4,500	6,000	30,000	38,000
16	Henequen	4.9 ± 0.07	6.0 ± 0.15	4.6	4.3	5.1	6.3	5.5	5.2	1,350	1,900	1,900	2,200	16,000	19,000
17	do	4.4 ± 0.08	5.4 ± 0.09	4.8	4.3	5.9	5.4	5.0	5.8	1,750	2,100	2,500	2,900	44,000	54,000
18	Pita floja	3.4 ± 0.09	3.6 ± 0.10	2.4	2.3	3.4	4.1	3.0	3.2	275	1,250	150	250	220	370
19	Jute	1.7 ± 0.07	1.5 ± 0.08	1.3	1.3	1.4	1.8	1.2	1.5	420	710	200	250	2,500	3,200
20	do	1.3 ± 0.04	1.3 ± 0.06	1.3	1.1	1.0	1.8	1.2	1.7	560	620	170	190	1,000	1,050
21	Hemp	1.5 ± 0.10		2.2	1.6	1.8	2.0	1.8	2.3	320	1,250	250	350	650	950
22	do	2.4 ± 0.12	2.3 ± 0.12	2.6	1.3	2.3	1.5	2.2	2.3	200	200	225	225	775	775
23	do	1.5 ± 0.06	1.4 ± 0.06	1.0	1.0	1.3	1.3	1.3	1.5	200	150	125	100	425	350
24	Roselle	1.7 ± 0.07	2.1 ± 0.10	1.8	1.7	1.4	1.5	1.5	1.4	190	225	270	300	4,250	4,600
25	Manzanita	1.6 ± 0.05	1.6 ± 0.06	1.2	1.2	1.2	1.1	1.2	1.3	450	330	110	85	1,850	1,450
26	Malvita	0.9 ± 0.04	1.3 ± 0.05	1.0	1.0	1.1	0.9	1.1	1.1	430	300	230	150	9,600	6,500
27	Roselle	1.7 ± 0.06	1.8 ± 0.06	1.4	1.4	1.5	1.3	1.4	1.5	400	450	255	285	3,600	4,100
28	Sansevieria	4.7 ± 0.25													
29	do	3.5 ± 0.14													
30	do	[c] 4.1 ± 0.13													
31	do	3.7 ± 0.15													
32	Yucca	[c] 4.3 ± 0.14													
33	do	[c] 4.6 ± 0.21													
34	Ixtle	4.5 ± 0.15													
35	Palmetto	[c] 1.7 ± 0.09	[c] 1.0 ± 0.10							100					

[a] SS indicates an S-twist in the bundle of fibers and an S-twist in the ply of two bundles.
[b] SZ indicates an S-twist in the bundle of fibers and a Z-twist in the ply of two bundles.
[c] Standard error, see footnote a of table 1.

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V. DISCUSSION OF RESULTS

1. FINENESS OF FIBER

The average number of fibers per bundle varied from about 2 for sisal, henequen and palmetto, to 500 for jute. The fineness o fiber varied from about 30,000 ft/lb for the coarser fibers to over 800,000 ft/lb for the fine jute fiber. The variation in fineness of fiber was great for a given kind of fiber. It ranged, for example, from 49,000 to 96,000 ft/lb for abaca, 33,000 to 65,000 ft/lb for sisal, and 165,000 to 280,000 ft/lb for hemp.

2. BREAKING STRENGTH AND ELONGATION, DRY AND WET

The breaking length expresses the breaking strength per uni weight of unit length of the bundle of fibers. The values given in table 1 for the bundle are lower than the values which would be obtained for the single fiber, because the strength of the fiber is

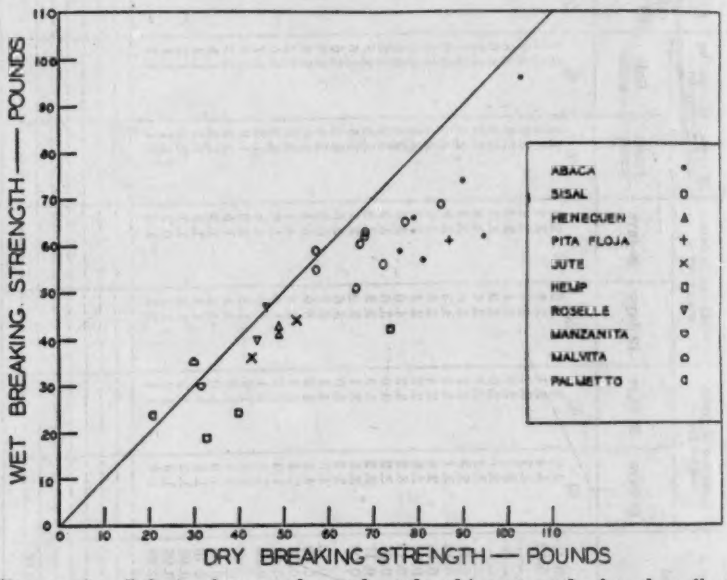

FIGURE 8.—*Relation between dry and wet breaking strength of cordage fibers.*

not fully realized when a group of fibers are tested simultaneously as in a bundle of fibers. The breaking lengths of the abaca fiber for the bundle, table 1, range from 138,000 to 180,000 ft. The average breaking length of different grades of abaca determined from tests of individual fibers ranged from about 175,000 to 250,000 ft, according to Becker.[1] On the other hand, and for the same

[1] Genevieve Becker, *Color of abaca fiber in relation to deterioration by weathering*, Cord Age 28, 24, 26, 2 and 30 (Dec. 1938).

reason, the breaking lengths for the bundle of fibers are higher than those which would be obtained for ropes made from these fibers. The values obtained in this laboratory by Mease [2] for a variety of sizes of rope made from different grades of abaca ranged from 32,000 to 56,000 ft. The breaking lengths for the bundle, however, give a good indication of the relative intrinsic strength of the various fibers. The strength of ropes made from these fibers would be expected to be in the same relative order. A variation in the relative order would indicate either a more or a less efficient realization of the strength of the bundle of fibers when made into rope. Whether or not the strength of the bundle of different kinds of fibers is realized to varying degrees in ropes can only be determined by tests of bundles of fibers and ropes made from them.

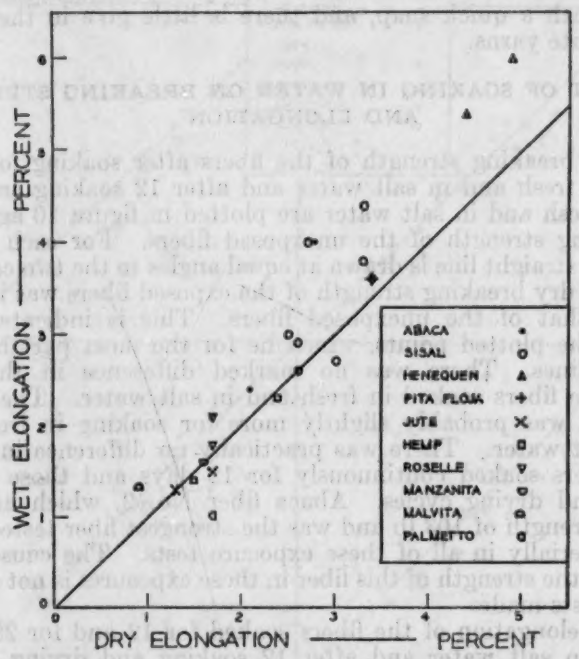

FIGURE 9.—*Relation between dry and wet elongation of cordage fibers.*

The wet strength of the bundles of fibers was in general lower than the dry strength. This is clearly shown in figure 8 where the wet strength is plotted against the dry strength. The plotted points are for the most part below the straight line drawn at equal angles to the two coordinate axes. Since the points for a given kind of fiber are considerably scattered, no definite advantage of one kind of fiber over the other is indicated with respect to dry versus wet strength.

[2] Unpublished data.

The wet elongation of the bundles of fibers was in general greater than the dry elongation. This is indicated in figure 9 where the wet elongation is plotted against the dry elongation. The plotted points lie for the most part above the straight line drawn at equal angles to the two coordinate axes. The henequen fibers had the highest elongation of the fibers tested, although their strength was less than for many of the other fibers. The jute fibers, which had approximately the same strength as the henequen fibers, were among those fibers having the lowest elongation. On the basis of these results, henequen would be superior to jute in its ability to withstand impact loads. The low stretch, and therefore low impact strength, of jute yarns has long been recognized. The extensive use of jute for wrapping twine by the United States Post Office Department is attributed to these characteristics. The jute yarn is readily broken by hand with a quick snap, and there is little give in the package tied with jute yarns.

3. EFFECT OF SOAKING IN WATER ON BREAKING STRENGTH AND ELONGATION

The dry breaking strength of the fibers after soaking for 12 and 28 days in fresh and in salt water and after 12 soaking and drying cycles in fresh and in salt water are plotted in figure 10 against the dry breaking strength of the unexposed fibers. For each exposure condition a straight line is drawn at equal angles to the two coordinate axes. The dry breaking strength of the exposed fibers was in general less than that of the unexposed fibers. This is indicated in the figure by the plotted points, which lie for the most part below the 45-degree lines. There was no marked difference in the results between the fibers soaked in fresh and in salt water. The decrease in strength was probably slightly more for soaking in fresh water than in salt water. There was practically no difference in strength for the fibers soaked continuously for 12 days and those given 12 soakings and drying cycles. Abaca fiber No. 2, which had a dry breaking strength of 103 lb and was the strongest fiber tested, deteriorated materially in all of these exposure tests. The cause for the decrease of the strength of this fiber in these exposures is not apparent from the tests made.

The dry elongation of the fibers soaked for 12 and for 28 days in fresh and in salt water and after 12 soaking and drying cycles in fresh and in salt water is plotted in figure 11 against the dry elongation of the unexposed fibers. For each exposure condition a straight line is drawn at equal angles to the two coordinate axes. The dry elongation of the exposed fibers was in general slightly greater than that of the unexposed fibers. This is indicated in the figure by the plotted points, which lie for the most part above the 45-degree lines. There was no marked difference in the results between the fibers soaked in fresh and in salt water. The increase in elongation is probably slightly less for fibers soaked in fresh water than in salt water. There was practically no difference in elongation for the fibers soaked continuously for 12 days and those given 12 soaking and drying cycles.

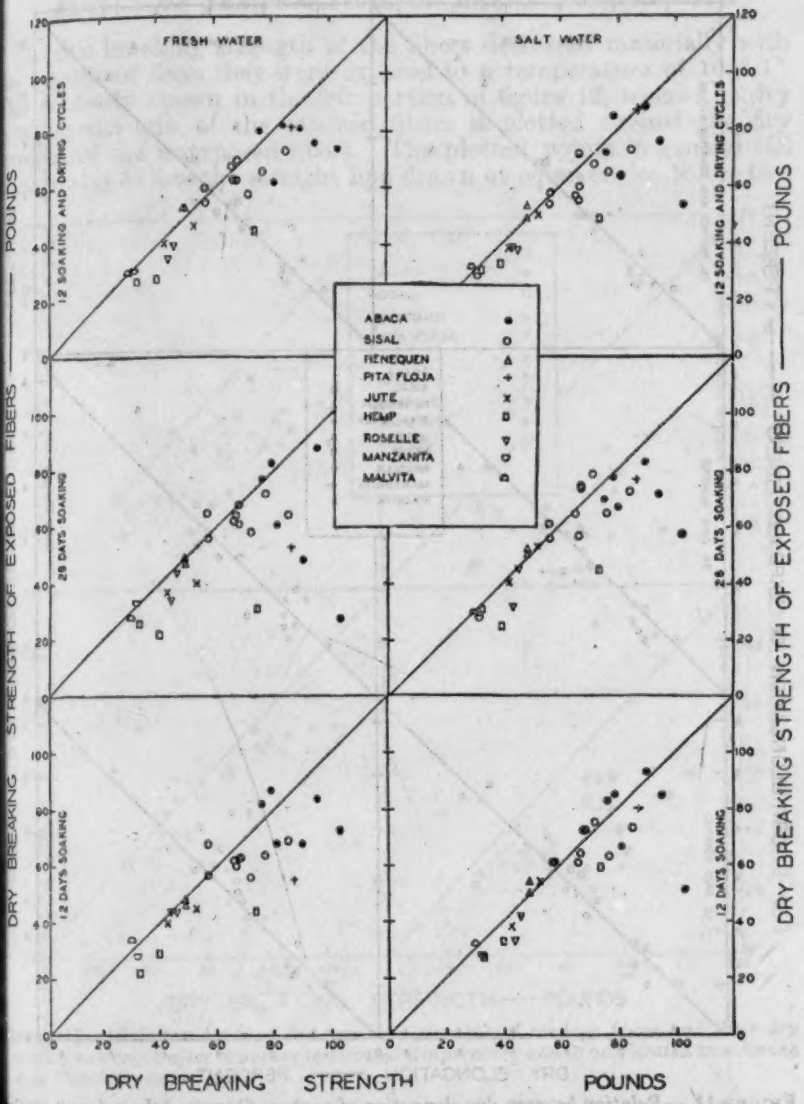

FIGURE 10.—*Relation between dry breaking strength of cordage fibers and their dry breaking strength after soaking in fresh and in salt water.*

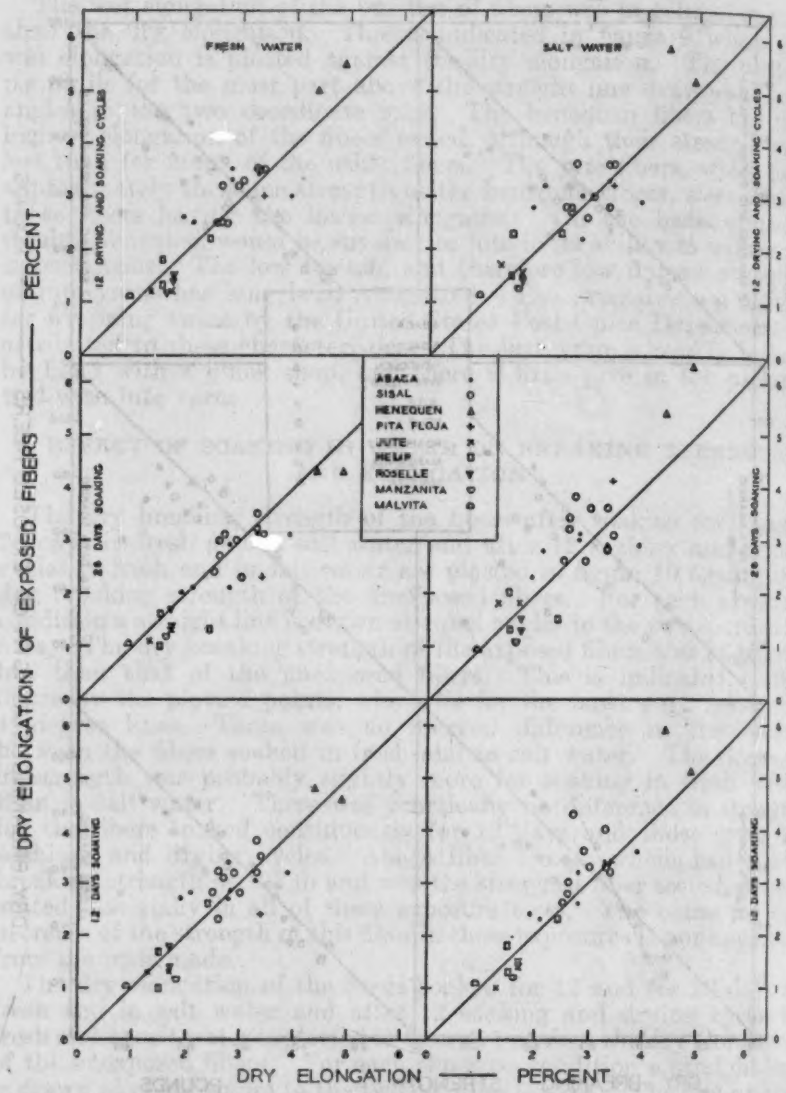

FIGURE 11.—*Relation between dry elongation of cordage fibers and their dry elongation after soaking in fresh and in salt water.*

4. EFFECT OF TEMPERATURE ON BREAKING STRENGTH

The dry breaking strength of the fibers decreased materially with the number of days they were exposed to a temperature of 105° C. This is clearly shown in the left portion of figure 12, where the dry breaking strength of the exposed fibers is plotted against the dry strength of the unexposed fibers. The plotted points in general fall considerably below the straight line drawn at equal angles to the two

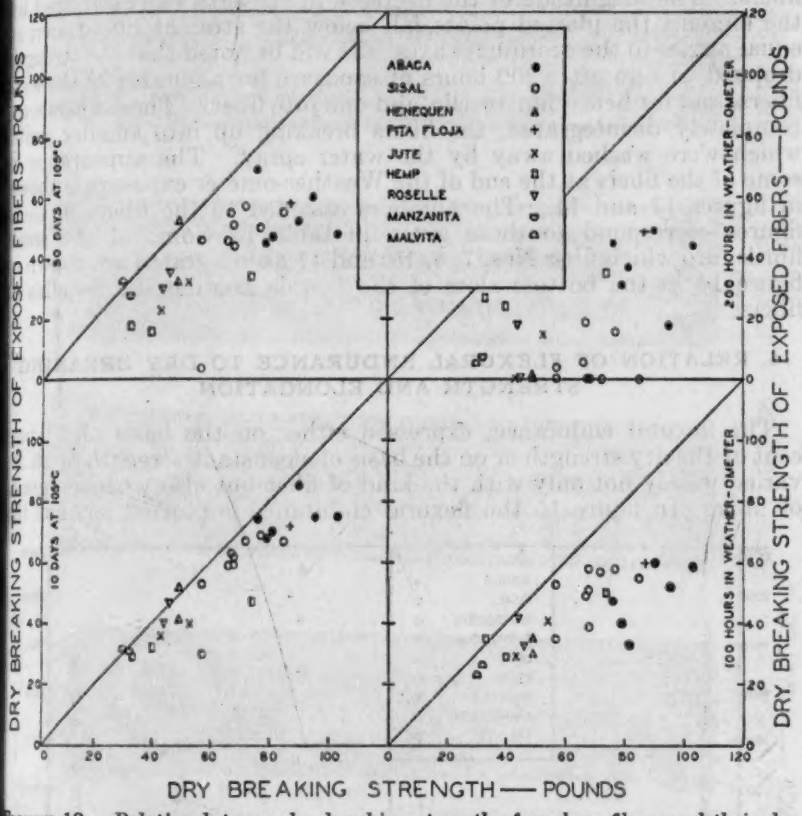

FIGURE 12.—*Relation between dry breaking strength of cordage fibers and their dry breaking strength after exposure to elevated temperature and to accelerated weathering in a Weather-ometer.*

coordinate axes. This was especially true after 30 days of exposure. Abaca fiber No. 2, in particular, dropped to less than 50 percent of its unexposed dry strength. This decrease in strength is comparable to that noted in the previous section for this fiber. The decrease in strength of sisal No. 12 was exceptionally large, amounting to 47 percent and 93 percent after 10 days and 30 days of exposure, respectively.

5. EFFECT OF ACCELERATED WEATHERING ON BREAKING STRENGTH

The dry breaking strength of the fibers decreased markedly with the number of hours of exposure to light and intermittent spraying with fresh water in the Weather-ometer. This decrease is shown in the right portion of figure 12, where the dry breaking strength of the exposed fibers is plotted against the dry strength of the unexposed fibers. The magnitude of the decrease in strength can be judged by the amount the plotted points fall below the straight line drawn at equal angles to the coordinate axes. It will be noted that the strength dropped to zero after 200 hours of exposure for a number of the sisal fibers, and for henequan, roselle, and one jute fiber. These fibers were completely disintegrated, the fibers breaking up into smaller units which were washed away by the water spray. The appearance of some of the fibers at the end of the Weather-ometer exposure is shown in figures 13 and 14. The numbers assigned to the fibers in these figures correspond to those given in table 1. Some of the small fibrils into which fiber Nos. 7, 8, 10, and 17 disintegrated are shown in figure 14 in the bottom slots of the boards holding the bundles of fibers.

6. RELATION OF FLEXURAL ENDURANCE TO DRY BREAKING STRENGTH AND ELONGATION

The flexural endurance, expressed either on the basis of 50 percent of the dry strength or on the basis of a constant strength of 20 lb varied widely not only with the kind of fiber but also with the grade of fiber. In figure 15 the flexural endurance is plotted against the

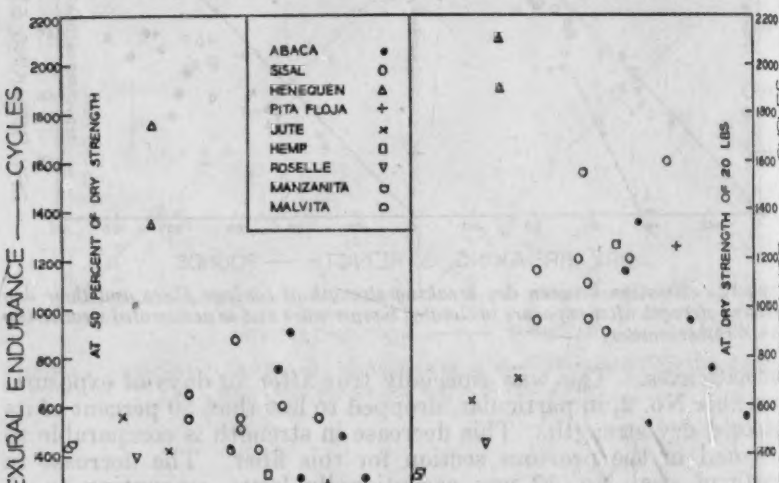

FIGURE 15.—*Relation between dry breaking strength of cordage fibers and their flexural endurance.*

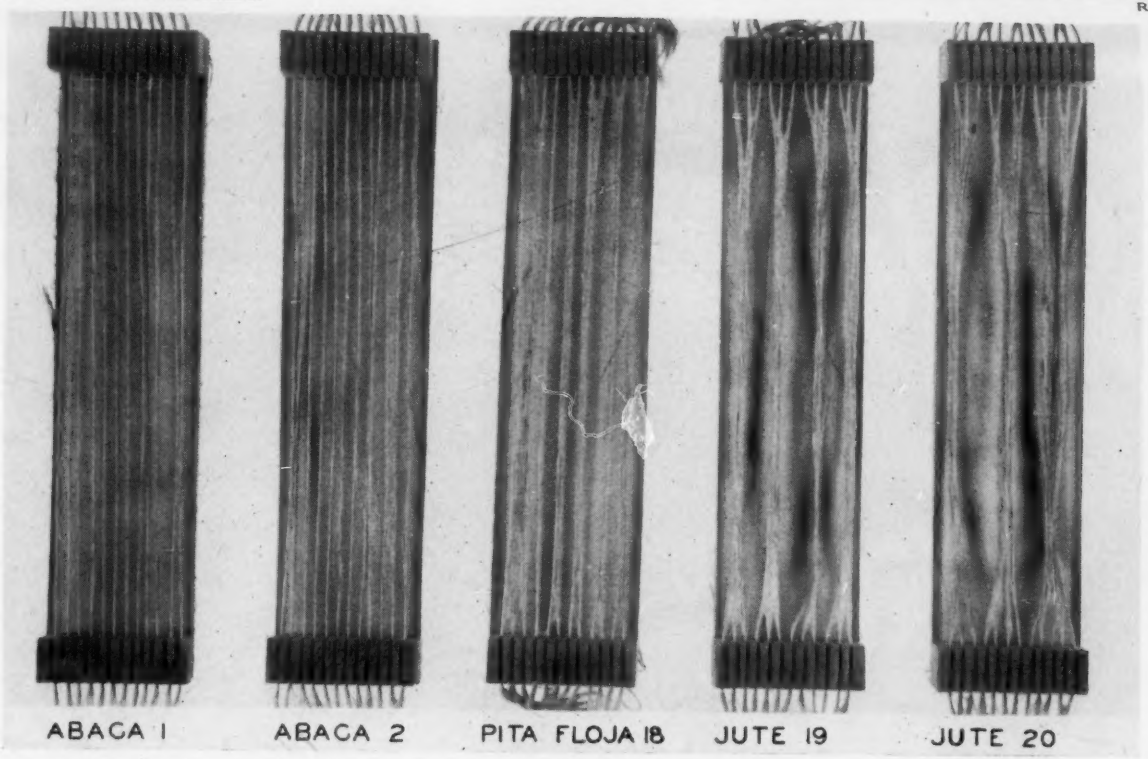

FIGURE 13.—*Appearance of abaca, pita floja, and jute fibers after 183 hours' exposure in Weather-ometer.*

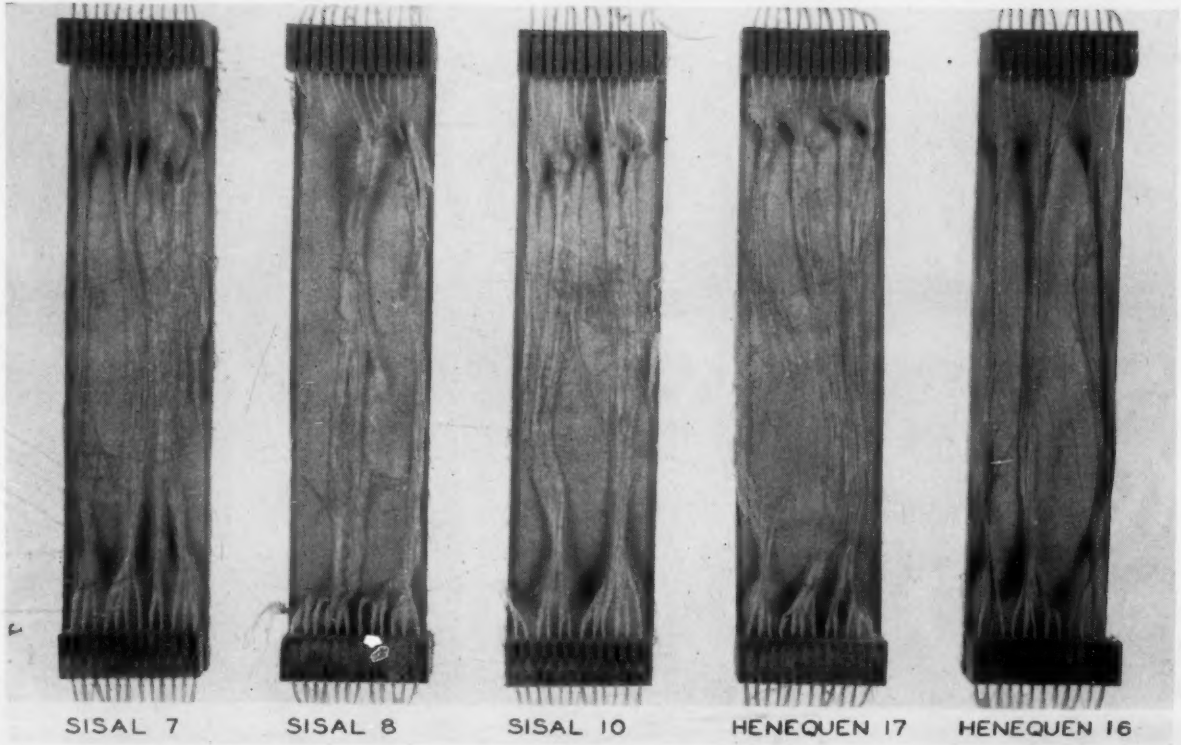

FIGURE 14.—*Appearance of henequen and sisal fibers after 183 hours' exposure in Weather-ometer.*

dry breaking strength of the fibers. The plotted points show no definite correlation between the flexural endurance and dry strength. The flexural endurance of henequen was considerably greater than for the other fibers. Since the elongation of the henequen fiber was also considerably greater than for the other fibers, a correlation between flexural endurance and elongation is indicated. The flexural endurance is plotted in figure 16 against the dry elongation of the fibers. In general, the flexural endurance increased with the intrinsic elongation of fibers, relative freedom of movement of the structural units within the fibers. This result is in substantial agreement with the effect of relative freedom of movement of the fibers in a yarn, and of yarns in a fabric on the folding endurance of fabrics.[3] Fibers having a high elongation, such as nylon, should greatly excel in flexural endurance any of the cordage fibers tested.

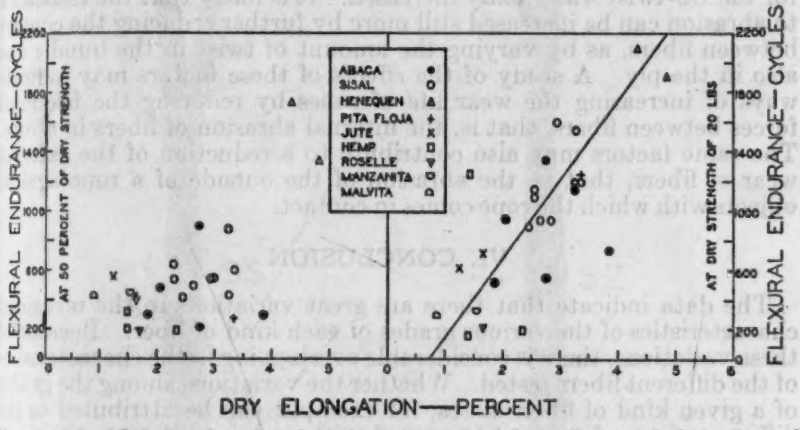

FIGURE 16.—*Relation between dry elongation of cordage fibers and their flexural endurance.*

7. RESISTANCE TO ABRASION

(a) S-TWIST IN THE BUNDLE AND IN THE PLY

The resistance to abrasion of the fibers for the SS-twist, that is, S-twist in the bundle of fibers and an S-twist in the ply of two bundles, varied over a great range. The results do not seem to correlate with any of the other fiber properties measured, except fineness of fiber. The resistance to abrasion of fibers 1 to 15, inclusive, all of which are classed as hard fibers, is very much higher than that of fibers 16 to 27, inclusive, all of which are classed as soft fibers. The fineness of fiber, expressed in feet per pound, of the hard fibers is very much smaller than for the soft fibers.

(b) S-TWIST IN THE BUNDLE AND Z-TWIST IN THE PLY

The resistance to abrasion of the fibers for the SZ-twist, that is, S-twist in the bundle of fibers and a Z-twist in the ply of two bundles, also varied over a great range. The results did not fall into two dis-

[3] Herbert F. Schiefer and Paul M. Boyland, *Note on flexural fatigue of textiles*, J. Research NBS **29**, 69 (1942) RP1485.

FIGURE 14.—*Appearance of henequen and sisal fibers after 183 hours' exposure in Weather-ometer.*

tinct groups as for the SS-twist. The resistance to abrasion for some of the soft fibers exceeded that for some of the hard fibers. The results do not seem to correlate with any of the other characteristics measured.

The resistance to abrasion for the SZ-twist was very much greater in general than for the SS-twist. This large difference is attributed to the difference in contact between the fibers of the two bundles for the two twists. In the SS-twist the fibers of the two bundles are essentially parallel, and therefore make contact for a considerable distance along the length of a fiber. The opposite is true for the SZ-twist, in which the fibers of the two bundles cross each other. This difference in alignment of the fibers for the two twists is shown in figure 17. It is apparent that the resistance to abrasion depends upon the contact and frictional force between the fibers. It was found that if a small amount of lubricant was added to the fibers, the resistance to abrasion for the SS-twist was greatly increased. It is likely that the resistance to abrasion can be increased still more by further reducing the contact between fibers, as by varying the amount of twist in the bundle and also in the ply. A study of the effects of these factors may indicate ways of increasing the wear life of ropes by reducing the frictional forces between fibers, that is, the internal abrasion of fibers in a rope. The same factors may also contribute to a reduction of the external wear of fibers, that is, the abrasion of the outside of a rope against objects with which the rope comes in contact.

VI. CONCLUSION

The data indicate that there are great variations in the measured characteristics of the various grades of each kind of fiber. Because of these variations, there is considerable overlapping in the characteristics of the different fibers tested. Whether the variations among the grades of a given kind of fiber, abaca, for example, can be attributed to the difference in grade cannot be stated with certainty, because some of these fibers had been stored for a number of years. The baling dates for the abaca fiber ranged for 1941 to 1936, that is, 2 to 7 years before the fibers were tested. Abaca fiber No. 2, which was baled in 1941, was considerably stronger than those baled in 1936, namely, fibers 3, 4, 5, and 6. Although abaca had the highest strength of the fibers tested, several grades of sisal, pita floja, and sansevieria were stronger than some of the grades of abaca. The abaca fiber, which had the highest dry breaking strength, was the third weakest after 28 days of soaking in fresh water.

The henequen fibers had the highest elongation. Although their dry strength was only about half of that of the abaca, they had the highest flexural endurance. They were affected little by exposure to elevated temperature, but disintegrated completely upon exposure to light and intermittent spraying with water. Sisal also disintegrated in this test and the breaking strength of the remaining fibers was drastically reduced.

The resistance to abrasion was highest for henequen and sisal. Pita floja, which is one of the strongest fibers tested, was among the lowest in resistance to abrasion. The resistance to abrasion of the fibers tested was profoundly affected by the direction of twist in the ply

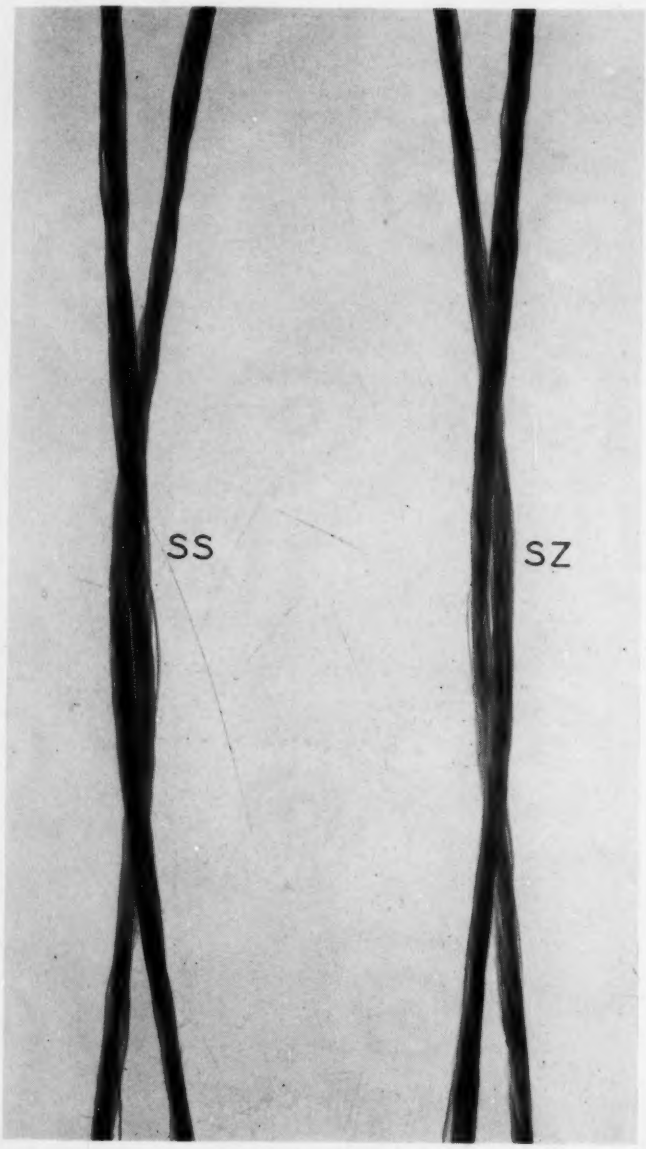

FIGURE 17.—*Alinement of fibers for* SS*–twist and* SZ*–twist of the abrasion tests.*

relative to that in the bundle, and also by the addition of a small amount of lubricant.

Sansevieria had exceptionally good dry strength. Sufficient material was not available for making the other tests on sansevieria. Hemp and jute were very similar in all the characteristics measured.

The testing machines and methods described in this paper are thought to be suitable not only for a quick evaluation of the characteristics of new or experimental fibers, usually available only in small quantities, but also for a systematic and comprehensive investigation of the characteristics of all grades and kinds of cordage fibers. A correlation study of the results of tests of fibers with the results of tests of cordage and rope made from the same fibers might contribute materially to the production of more uniform and durable products, especially those suitable for specific uses requiring high impact strength, high flexural endurance, or high resistance to internal and external abrasion. Since the machines and methods are applicable for testing small quantities of fiber, such as from a single leaf, they should prove useful in the evaluation of agricultural experiments for growing improved cordage fibers or in the evaluation of chemical treatments and processing of the fibers.

The author expresses his appreciation to Betty J. Skrdla, Jean Persons, Dorothy Rundles, and Philip Miller for carefully preparing the large number of bundles of fibers and for making the numerous tests of the various characteristics of the fiber. The assistance of Gladys White in the preliminary experiments and in checking some of the computations and that of Josephine Blandford in the preparation of the graphs is gratefully acknowledged. Finally, the cooperation of the American Manufacturing Co., Boston Navy Yard, Hooven & Allison Co., Plymouth Cordage Co., U. S. Department of Agriculture, Wall Rope Works, and Whitlock Cordage Co. in furnishing most of the fibers for the tests is appreciated.

WASHINGTON, June 23, 1944.

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